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Sediment Sampling in Ponds A8w and A8d
Former Cargill Salt Ponds
Lower Guadalupe River Flood Control Project
Alviso, CA

Prepared for

Mr. Terry Neudorf, Environmental Planner II

Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118-3614

Prepared by:

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State EPA R.E.A. Number 04072
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March 17, 2004
LA&S Project No. 0398

Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, California 95118-3614

Attn.: Mr. Terry Neudorf, Environmental Planner II

Re: Mercury Sediment Background Sampling Report, Lower Guadalupe River Flood Protection Project, Alviso, California

Dear Mr. Neudorf,

Light Air and Space Construction (LA&S) has prepared this Mercury Sediment Sampling on Ponds A8w and A8w, Lower Guadalupe River Flood Protection Project on the behalf of the Santa Clara Valley Water District (SCVWD) for the above referenced site. If you have any questions, please call.

Sincerely,
Light, Air and Space Construction

David B. Guthridge
Principal

Christopher M. Palmer
CHG 246; CEG 1262

REGISTERED GEOLOGIST
CHRISTOPHER M. PALMER
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Cc: Mr. Clyde Morris, US Fish and Wildlife Service (1 copy)

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TABLE OF CONTENTS

		PAGE
	Executive Summary	2
1.0	Background and Technical Approach	3
2.0	Sample Location Rationale and Location Selection	4
3.0	Pre-field Activities, FWS Permit and Safety Plan	5
4.0	Field Methods-Sediment Sampling	6
	4.1 Sediment Sampling Procedures	6
	4.2 Sampling Deviations	6
	4.3 Sample Documentation	7
	4.4 Sample Containers Preservation and Shipment	7
5.0	Chemical Analysis	8
	5.1 Quality Assurance and Quality Control QA/QC Methods	8
6.0	Field Conditions	9
7.0	Chemical Analytical Sample Results and Discussion	11
	7.1 Quality Control Comments	12
	7.2 Discussion	12
8.0	Conclusions	14
9.0	Limitations	15
10.0	References	15

Tables

Table 1. Pond Field Sampling location Summary, February 11, 2004
Table 2. Pond Water Quality Field Sampling Summary, February 11, 2004
Table 3. Sediment Analytical Data

Appendices

Appendix 1. Figures
Figure 1. Location Map
Figure 2. Sample Location Map
Appendix 2. Site Photographs
Appendix 3. U. S. Fish and Wildlife Conditional Use Permit Information
Appendix 4. Chemical Analytical Reports and Chain-of-Custody and Sample Analytical Methods and QC Documents

Executive Summary

Light Air and Space Construction performed sediment sampling in the former Cargill Salt Ponds near Alviso, California. The purpose of this sampling was to gather background sediment data on the presence of Mercury and Methyl Mercury in Ponds A8w and A8d as a portion of the San Francisco Bay Regional Water Quality Control Board (RWQCB) request to monitor floodwaters and suspended sediments that could enter the salt ponds. The purpose of the plan is to determine the concentration of mercury in lower Guadalupe River floodwaters to determine whether they exceed the TMDL objective concentration.

Sediment was sampled on February 11, 2004 in the Ponds. Pond A8w was flooded and Pond A8d was partially dry at the time of sampling. The Ponds are thought to have been constructed in the 1920s, using dredged mud to create channels and piling the dredged mud to form the dikes between the Ponds. What appear to be natural channels are present on the Ponds bottoms, indicating that the Pond areas did not appear to be have been much altered during their dike construction.

Seventeen locations were sampled in the Ponds. The sediment in the pond bottoms is silty clay, with the surrounding dikes constructed of dredged clay and concrete debris. Pond A8w was flooded and Pond A8d was mostly dry with localized standing water during the sampling. The chemical analysis of the sediment revealed the following:

- Total Mercury was present at all 17 sample locations and Methyl Mercury was present at 14 locations.
- The highest level of Methyl Mercury occurred in samples A8W-2, A8W-3, A8W-6, and A8W-10 at over one ng/g.
- The general trend from these limited data appear to indicate slightly more Methyl and Total Mercury, and more basic pH conditions in Pond A8w compared to Pond A8d. A possible interpretation of these trends might be due to year-round presence of water in a majority of the area of Pond A8w and extended periods of dryer conditions with limited areas of water standing water in Pond A8d.
- Additional sampling data collected from Ponds A8w and A8d, as well as regional sampling data from the adjacent ponds would aid the understanding of the presence of Mercury and Methyl Mercury trends in the area.

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1.0 Background and Technical Approach

The SCVWD has been tasked with developing and implementing a mercury monitoring plan in consultation with the San Francisco Bay Regional Water Quality Control Board (RWQCB) to monitor floodwaters and suspended sediments that could enter the salt ponds. The purpose of the plan is to determine the concentration of mercury in lower Guadalupe River floodwaters to determine whether they exceed the Total Maximum Daily Load (TMDL) objective concentration. The information would then be used to determine whether corrective actions are needed in Cargill Ponds (A5, A6, A7, A8w and A8d, area roughly bounded by the Alviso Slough and Guadalupe Slough) to reduce mercury concentrations. There has apparently never been a previous mercury soil-sampling program in the ponds or near the weir. This sediment sampling was conducted at existing salt production ponds (designated hereafter as Ponds A8w and A8d).

RWQCB stated that short term monitoring would include annual site inspections during years one to five following the project construction. The overall approach to monitoring of accumulation of mercury in sediments in Cargill Salt Ponds during the short-term monitoring period will include:

- Collection of background mercury concentration data in salt pond sediments.
- Collecting background mercury concentrations in large flows in the Guadalupe River.
- Collecting water and sediment concentration data and depth of accumulation data if a flood occurs that is large enough to flow into Cargill Ponds.

The purpose of this work was to collect initial background chemical data sediment samples over the area of Ponds A8w and A8d. The samples were collected to ascertain presence of mercury concentrations as a background in shallow pond sediments.

Samples were collected using a random stratified sampling grid since there has not been previous mercury sampling. This type of sampling grid may be used to estimate trends of patterns of contaminants and the approach is to acquire initial data on the presence of mercury in the shallow sediment in the ponds. Each pond was subdivided into approximately equal areas and one sample was collected as near to the center of the individual grid as possible given conditions at the time of the sampling. After review of the approach with the SCVWD representative, 17 areas in the Ponds were selected for sampling.

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2.0 Sample Location Rationale and Location Selection

The purpose of the sampling plan was to attempt to gain an initial view of the background mercury concentration in the shallow pond sediment in Ponds A8w and A8d (see Appendix 1, Figures 1 and 2 and Appendix 2, Site Photographs). A random stratified grid was placed across the ponds to allow for sample location within each grid. The number of sample locations depends upon the type of water body and removing some sampling bias from the samples in analytical approach. This initial sampling used a minimum number of samples selected to cover the area.

The sample depths were targeted to collect sediment recently deposited in the ponds (typically the uppermost six to 12 inches of sediment. Information on sedimentation rates in the ponds is not available for this work. Cargill has apparently moved water for the salt-brine purposes around the ponds for years but "natural" flood events and sedimentation information resulting there from is not available. Therefore, the uppermost sediment layer (zero to six-inches below the surface or base of the pond) was sampled for this work.

The sampling approach used techniques discussed in Hakanson and Jansson (2002) for selecting the estimated number of sediment samples. It was assumed that pond bottoms were essentially flat and there were canals around the pond perimeters. Another assumption was that the ponds were flooded and sedimentation would occur over the pond floor areas, with some sediment transportation through the existing canals, and that both transport and deposition would occur in the canals and the entrances and exits to the ponds.

The Hakanson and Jansson formula initially estimated six samples for all six ponds (total of 32 samples). The District decided to limit the sampling to Ponds A8w and A8d. A review by the District indicated that they did have some background data for other ponds that was not provided to LA&S for use in this report. Consequently, the sampling plan was revised for sampling only Ponds A8w and A8d for a total of 17 locations.

A sample grid was drawn over the maps of the ponds and one sediment sample was collected from within the roughly equal-sized sample grid areas that yielded a total of seventeen (17) sediment samples over the irregularly shaped ponds. A Magellan hand-held Global Positioning System device (GPS) was used to locate the sampling positions. Samples were collected in the uppermost sediment strata at depths of zero to six inches below the water/pond floor interface and/or six (6) inches below the pond floor; this depth was assumed representative of sedimentation in the ponds in the recent past. Some sampling deviations occurred and are discussed below.

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3.0 Pre-field Activities, FWS Use Permit and Safety Plan

The U. S. Fish and Wildlife Service (FWS) rigorously controls access to all salt ponds areas since the site is located within the Don Edwards National Wildlife Refuge (Refuge). SCVWD gate keys allow initial entrance, but FWS Refuge keys are needed to access the old salt pond levee roads. The access roads and paths are limited, so both overland traversing (where feasible and safe) and sampling from a boat, in the ponds was necessary. The FWS required an approved use permit to access and perform this sediment sampling prior to entering the site and the Permit is attached in Appendix B. The Special Use Permit number is 11640-2003-052. Due to delays in collecting equipment and weather, LA&S contacted Mr. Clyde Morris of FWS regarding delays and informed him of the actual field-sampling day. The conditional use permit request sent to FWS and a copy of the Permit is attached in Appendix 3.

A Site Health and Safety Plan (SHSP) was prepared for the sampling event. The SHSP outlined the work, type of work and safety gear needed and anticipated sampling conditions. A representative of the Cargill Salt Company was contacted regarding movement around and in the ponds. The Cargill representative informed LA&S that movement on foot on the "dry" pond floors was potentially dangerous due to thin and unstable crusts through which one may sink into the mud. It was strongly recommended to LA&S by the Cargill representative that sampling from a flat-bottom boat was preferable. The Cargill representative assisted LA&S with information on pond depths, depth of water and on traversing pond bottoms and a brief history of the ponds.

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4.0 Field Methods –Sediment Sampling

4.1 Sediment Sampling Procedures

Sediment samples were collected from the locations using hand coring from the surface using a pre-cleaned trowel or drive core sampling from a boat in the flooded areas. All drilling equipment and sampling tools were cleaned prior to arriving, after use at each sampling location and before leaving the site. Hand cored samples were placed in brass sampling liners until no headspace remained, the ends were then sealed with Teflon tape and plastic endcaps, the liners were labeled, the brass liner information entered onto a Chain-of-Custody and the sample liners were then placed in a zip-lock plastic bag and placed on crushed ice in an ice chest for transport to a State Certified analytical laboratory. The drive-sampler used from the boat was retrieved and dissembled, the soil filled brass liner was sealed with Teflon tape and plastic endcaps, the liner was then labeled, the brass liner information logged onto the Chain-of-Custody forms and the liner placed in a zip-lock plastic bag and placed on crushed ice in an ice chest for transport to a State Certified analytical laboratory.

Sediment soil samples in Pond A8d were collected on foot and in Pond A8w were collected from an inflatable boat. At the time of work plan preparation, the depth of water in the ponds was unknown, but was estimated by Cargill to vary from several inches to several feet depth depending upon the location. Several "canals" exist along the pond access roads and water depth in these varies at least several feet deep.

Field data was collected on field sheets to document the sampling location. The shallow boreholes sediments were logged using the Unified Soil Classification System under the supervision of a registered geologist. When sampling in flooded ponds field water quality measurements were collected at the sampling location using a Horiba U-10 Field Measuring device, which was calibrated prior to being used in the field. Water quality measurements included pH, dissolved oxygen, oxidation-reduction potential, salinity, temperature, conductivity, and specific gravity of seawater. Additional lithologic and descriptive information will be collected to describe the sediment at each sample location. The shallow soil borings collected soil samples by penetrating into the sediment to depths of about six inches (see Tables 1 and 2).

4.2 Sampling Deviations

Some adjustments were made to sampling locations depending upon access, safety or wildlife/habitat considerations. Some of the pre-selected sample locations of Pond A8w were not accessible due to extremely shallow water conditions and samples were obtained from locations as near to the pre-selected locations as existing site conditions allowed (see Site Photographs in Appendix 2)..

Some sample locations were changed in Pond A8d to near the edge of the pond due to very soft mud conditions that caused the sample technician to begin to sink. The sample locations were moved north near the pond edge, but were all located within the northern half of the A8d Pond bottom, away from what appeared to be disturbed soil from levee or dike road construction at the surface.

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4.3 Sample Documentation

Each soil sample has a unique sample identity number. The samples collected from pond A8w were designated A8W-1 through A8W-12 and samples from Pond A8d were designated A8d-13 through 17. Two quality control samples were collected in a manner similar to the other samples, one sample from each Pond. The quality control sample from Pond A8w was designated A8W-18, and the quality control sample from Pond A8d was designated A8d-19.

4.4 Sampling Containers, Preservation and Shipment

Sediment sample liners were pre-cleaned by the commercial supplier or laboratory. Sample collection, handling and analytical request used standard chain-of-custody documentation to document possession and transfer of samples, with date and time related signatures. Chain-of-custody records track samples from the time of collection through receipt by the analytical laboratory. The chain-of-custody were prepared by the sampling technician in the field following the sample collection and accompanied the samples and cooler to the laboratory.

Sample coolers were used to pack the samples on crushed ice and were transported to the laboratory at the end of the sampling day. LA&S transported the Chain-of-Custody and cooler directly to the analytical laboratory.

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5.0 Chemical Analysis

Seventeen sediment samples were analyzed at Sequoia Analytical Laboratory, in Morgan Hill, California the contract SCVWD laboratory. The Methyl Mercury analyses were performed at Brooks Rand, LLC in Seattle Washington, the subcontractor laboratory for Sequoia. Samples were tested for the following; Sulfate (as SO4), pH, Total Organic Carbon, Total Mercury, and Monomethyl Mercury by EPA Methods 6000/7000, 415.1. Sequoia Analytical Laboratory provided their laboratory methods and quality control procedures that are attached to this report (see Appendix 4). The analyses were run on a normal turnaround basis. The analytical reports are attached and the data is presented in Table 3 below.

5.1 Quality Assurance and Quality Control QA/QC Methods

Two blank "sediment' samples were used to check equipment cleanliness and potential ambient air influences. A bag of commercially available fine-grained playground sand was brought to the site and left open during sampling work. Sand samples were sampled in the same manner as the true samples with identical packaging, labeling and handling procedures and designated as discussed above.

Data validation methods help verify that the data reported by the laboratory accurately represents the conditions encountered in the field. Laboratory data was compared with field observations and elevated detection limits, errors and inconsistencies in data if any were discussed with the laboratory and revised or rerun for verification as appropriate. Comments on the QC samples are presented below.

The state-certified laboratory performing the analyses also had their procedure and instrument QA/QC processes including method blanks, surrogates, matrix spike and matrix spike duplicates, laboratory duplicates and calibration checks (see methods in Appendix 4)

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6.0 Field Conditions

The salt ponds have been used for decades and there is little documented information on their construction. The Cargill representative related the following brief history of the ponds. Ponds A8w and A8d are thought to have been constructed sometime prior to about 1920. A dredge was moved in and excavated a canal at the approximate pond perimeter and used the dredged soil to create the dikes between the pond areas. Over the years concrete debris was used to form roads on the eastern and southern edge of the Ponds that are visible today. Bay water was then circulated through the ponds to fill them. Precipitation collects in the ponds. The amount of water discharge from the Pond bottoms is unknown. The remaining water evaporates although some water continues to circulate in the Pond. The Ponds had received a large quantity of rainfall in the weeks prior to sampling.

The Ponds were sampled on February 11, 2004. Pond A8w was completely flooded and Pond A8d was mostly dry with localized standing water during the sampling. The sediment in both Ponds appears to be a moderate to highly expansive silty clay with very minor amounts of very fine sand dispersed in the clay. Broken bivalve and gastropod shells attributed to bird feeding locally liter the surface and may occur in the sediment. The Pond's bottoms are nearly devoid of vegetation due to the salty conditions. Small white precipitates and salt crystals are occasionally visible near the Pond dike boundaries and pond floor in A8d.

All samples collected in Pond A8w were collected below the current standing water level. Sample locations in Pond A8d slowly filled with water during and after sampling. Additional stream channels thought to be original channels meander across various areas of the surface of A8d. The depth of these channels could not be measured due to soft muddy conditions, but were estimated at over two feet in some areas. Some deep areas encountered in Pond A8w were as deep as ten feet; it is unclear whether these are natural or dredged channels. The perimeter canals along the pond dikes are reported to vary from five to ten feet deep. The sample location data and sampling conditions are summarized in Tables 1 and 2 below.

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Table 1. Pond Field Sampling Location Summary, February 11, 2004

POND	LOCATION	TIME	LAT	LONG	WATER DEPTH FEET	COMMENTS
A8w	1	14:20	37 26.148	121 59.817	2	None
A8w	2	14:05	37 26.149	121 59.651	3	None
A8w	3	13:48	37 26.149	121 59.806	3	None
A8w	4	13:33	37 25.854	121 59.587	3	None
A8w	5	13:10	37 25.836	121 59.423	2	None
A8w	6	12:48	37 25.712	121 59.171	2	None
A8w	7	12:25	37 25.700	121 59.009	10	None
A8w	8	14:30	37 25.413	121 59.748	7	None
A8w	9	14:35	37 25.413	121 59.625	4	None
A8w	10	14:41	37 25.414	121 59.332	5	None
A8w	11	14:54	37 25.412	121 59.117	6	None
A8w	12	15:09	37 25.414	121 58.916	5	None
A8d	13	14:20	37 25.373	121 59.632	Surface dry	Saturated at 6"
A8d	14	13:40	37 25.368	121 59.435	Surface wet	None
A8d	15	13:05	37 25.345	121 59.331	Surface dry	None
A8d	16	12:55	37 25.337	121 59.125	Surface dry	Saturated at 6"
A8d	17	12:45	37 25.332	121 58.949	Surface dry	None

Table 1. Pond Water Quality Field Sampling Summary, February 11, 2004

LOCATION	TIME	TEMP C	PH	COND MMHO/ CM	TURB NTU	DO MG/L	SALINITY %	OX/ RED. POT.	TDS	OT
1	14:20	11.12	9.84	9.42	90	9.96	4	135	56	50
2	14:05	11.16	9.82	9.41	91	9.91	4	137	56	51
3	13:48	11.18	9.80	9.39	90	9.84	4	133	56	50
4	13:33	11.25	9.72	9.38	87	9.45	4	141	56	51
5	13:10	11.26	9.70	9.36	94	9.41	4	139	56	52
6	12:48	11.92	9.71	9.39	83	9.59	4	144	56	49
7	12:25	11.28	9.67	9.37	84	9.07	4	136	56	50
8	14:30	11.27	9.66	9.43	88	10.12	4	121	56	50
9	14:35	12.10	9.81	9.44	82	10.97	4	102	57	50
10	14:41	12.22	9.89	9.42	65	10.99	4	114	56	50
11	14:54	12.28	9.75	9.40	80	9.13	4	119	56	50
12	15:09	13.65	9.76	9.41	87	9.22	4	90	57	50

Ox Red Pot – Oxidation-reduction potential; Temp. C – Temperature in centigrade; pH – Acidity alkalinity units; NTU – Nephlameter Turbidity Units. TDS – Total dissolved solids; OT – Specific gravity of seawater.

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7.0 Chemical Analytical Sample Results and Discussion

A total of 19 samples were analyzed (17 collected from the Ponds and two quality control samples). The laboratory results are summarized below.

Table 3. Sediment Analytical Data

SAMPLE NO.	SULFATE AS S04	PH	TOTAL ORGANIC CARBON	TOTAL MERCURY	METHYL MERCURY
	Mg/kg	Units	Mg/kg	Mg/kg	Ng/g
Pond A8w					
A8W-1	1600	8.18	14000	0.40	0.020
A8W-2	1200	8.28	16000	1.1	12.100
A8W-3	1800	7.42	12000	1.3	2.600
A8W-4	2000	8.03	10000	0.67	0.048
A8W-5	2000	7.97	13000	0.86	0.686
A8W-6	1000	8.05	7400	0.10	1.490
A8W-7	1600	8.01	17000	0.17	0.020
A8W-8	890	8.23	12000	0.12	0.031
A8W-9	1700	7.90	20000	1.1	0.317
A8W-10	2300	8.06	8800	1.7	1.040
A8W-11	1700	8.44	16000	0.36	0.627
A8W-12	2100	8.05	12000	0.18	0.054
A8W-18	2500	5.44*	ND	ND	0.020
Pond A8d					
A8d-13	1500	6.72	3500	0.069	0.236
A8d-14	8000	6.80	8800	0.043	0.337
A8d-15	4000	6.88	18000	0.082	0.047
A8d-16	2700	6.81	12000	0.36	0.761
A8d-17	130	7.29	13000	0.72	0.174
A8d-19	140	7.45	ND	ND	0.045

Laboratory reports that the concentration of 0.020 for methyl mercury corresponds to "non-detect" and are reported at the MDL. Mg/kg – Milligrams per kilogram. Ng/g – Nannograms per gram. See Laboratory reports.
* - Sequoia reran the pH of this sample that showed a pH of 6.470, however this rerun of the analysis exceeded the hold time.

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The highest level of Methyl Mercury occurred in samples A8W-2, A8W-3 and A8W-6, A8W-10 at over one ng/g. Samples A8W-1, A8W-7 and A8d-13 showed non-detected. The Total Mercury levels appeared somewhat higher in Pond A8w as compared to Pond A8d. Measurements of pH were somewhat lower in Pond A8d than Pond A8w. Total Organic Carbon (TOC) levels appear relatively consistent in the Ponds.

7.1 Quality Control Comments

The quality control samples showed that Total Mercury and Methyl Mercury were not detected in either sample (A8W-18 and A8d-19). LA&S contacted Brooks Rand LLC, the laboratory that performed the Methyl Mercury analysis regarding the data from A8d-19. While the level of Methyl Mercury in A8d-19 was slightly above the detection limit it was below the method detection limit and is considered as 'not detected." The numbers on the samples were inadvertently transposed, however the data are correct as present in Table 3 and amended pages from Brooks Rand are attached.

TOC was not detected in either sample. Sulfate data for samples A8W-18 and A8d-19 were more varied that anticipated for both quality control samples. The variability in Sulfate levels might be influenced by sand mineralogy of the quality control sand used for the samples however the difference is unclear.

The pH value for A8W-18 (5.44) appeared anomolously depressed when compared to the other pH values. LA&S asked Sequoia to rerun that sample for pH. The second value was 6.47 although the sample was technically beyond the hold time. In our opinion, the original pH value may be a localized variation, however the pH values trend within the upper 6 to lower 8 range and represent current site conditions in our opinion.

7.2 Discussion

These general sample data trends appear to indicate slightly more Methyl and Total Mercury and more basic pH conditions in Pond A8w. The levels of Total Organic Carbon appear relatively consistent in the Ponds and are attributed to deposition of organic-rich clay sediment in the ponds. The area of Pond A8w is much larger than A8d and the relationship of the pond size to the data trends might be due to less water entering Pond A8d, however there is insufficient information for further interpretation in our opinion.

It is our understanding that some sediment samples had been previously collected in the area, however that data was unavailable for LA&S review. Since there were no nearby data for comparison, LA&S performed a very brief literature search that revealed one study of historic metals trends in the northern San Francisco Bay. Hornberger et. al, (1999) reported historic background levels of mercury (assumed total mercury) at 0.06+/-0.01 ng/g. This apparently represented a decrease from 0.3 ug/g from the 1970s and suspect sources from a lead smelter in the area that may have contributed to that higher mercury number. It is unclear from the available information how these northern San Francisco Bay background concentrations reported by Hornberger might relate to the ponds.

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LA&S located a U. S. Geological Survey Open File Report (1971) that presents distribution of Mercury sampled in surface sediments (to depths of about four inches) in the San Francisco Bay Estuary. The data showed mercury concentrations of a median of 0.25 mg/kg and an average of 0.37 for the southern part of the Bay (south of Treasure Island). The total range of concentrations throughout the entire Bay estuary was 0.04 to 1.60 mg/kg. Mercury concentrations mapped near the extreme southern end of the Bay varied from 0.17 to 1.05 mg/kg.

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8.0 Conclusions

LA&S performed sediment sampling in the salt ponds designated A8w and A8d. These salt ponds were apparently constructed sometime prior to 1920 and have been in continuous use for salt production by the Cargill Salt Company. The ponds are currently included in the national wildlife refuge. The SCVWD has been tasked with developing and implementing a mercury monitoring plan in consultation with the San Francisco Bay Regional Water Quality Control Board (RWQCB) to monitor floodwaters and suspended sediments that could enter the ponds. The purpose of the plan is to determine the concentration of mercury in lower Guadalupe River floodwaters to determine whether they exceed the TMDL objective concentration. The sediment sampling was a part of this overall task.

Seventeen locations were sampled in the Ponds. The sediment in the pond bottoms is silty clay, with the surrounding dikes constructed of dredged clay and concrete debris. Pond A8w was flooded and Pond A8d was mostly dry with localized standing water during the sampling. The sediment chemical analysis revealed the following:

- Total Mercury was present at all 17 sample locations and Methyl Mercury was present at 14 locations.
- The highest level of Methyl Mercury occurred in samples A8W-2, A8W-3, A8W-6, and A8W-10 at over one ng/g.
- The general trend from these limited data appear to indicate slightly more Methyl and Total Mercury, and more basic pH conditions in Pond A8w compared to Pond A8d. A possible interpretation of these trends might be due to year-round presence of water in a majority of the area of Pond A8w and extended periods of dryer conditions with limited areas of water standing water in Pond A8d.
- Additional sampling data collected from Ponds A8w and A8d, as well as regional sampling data from the adjacent ponds would aid the understanding of the presence of mercury and methyl mercury trends in the area.

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9.0 Limitations

This report has been prepared specifically for the former Cargill salt ponds A8w and A8d near Alviso, CA and was done according to the current State and local agency suggested guidance documents for these investigations. The interpretations, conclusions and recommendations made herein are based on the data and analysis for the soil and water samples collected on-site, or other on-site reports and should be reviewed in the context of this report and other site reports. Conditions of the property can change over time and the use of this report by third parties is entirely at their own risk. Please note that reports of contamination must be submitted to the agencies in a timely manner. Light, Air and Space Construction is not responsible for errors neither in laboratory analysis and reporting, nor for information not available, nor unreported or unknown sources of site contamination during the course of the study, and no warranty or guarantee is expressed or implied therein.

10.0 References

Hornberger, M. I., Luoma, S. N., van Geen, A., Fuller, C. and Anima, R., 1999, Historic trends of metals of San Francisco Bay; core data from San Pablo Bay, Grizzly Bay, Richardson Bay and Central Bay: Marine Chemistry vol. 64, pg. 39-55.

Hakanson, L and Jansson M., 2002, "Lake Sedimentology": The Blackburn Press, Caldwell, New Jersey, 316 pg.

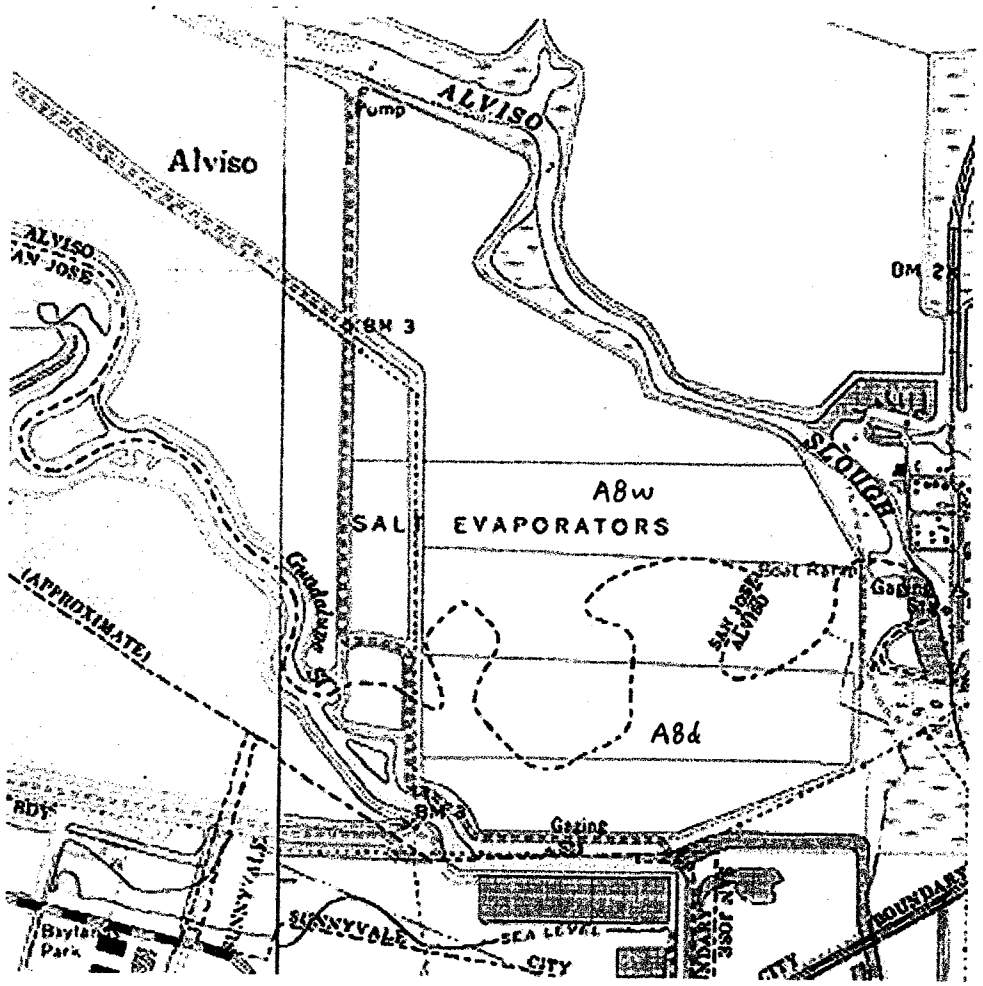
McCulloch, D. S., Conomos, T. J., Peterson D. H. and Leong, K., 1971, Distribution of mercury in surface sediments in San Francisco Bay Estuary, California: U. S. Geological Survey Open File Report, one map sheet.

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APPENDIX 1

Figures

N



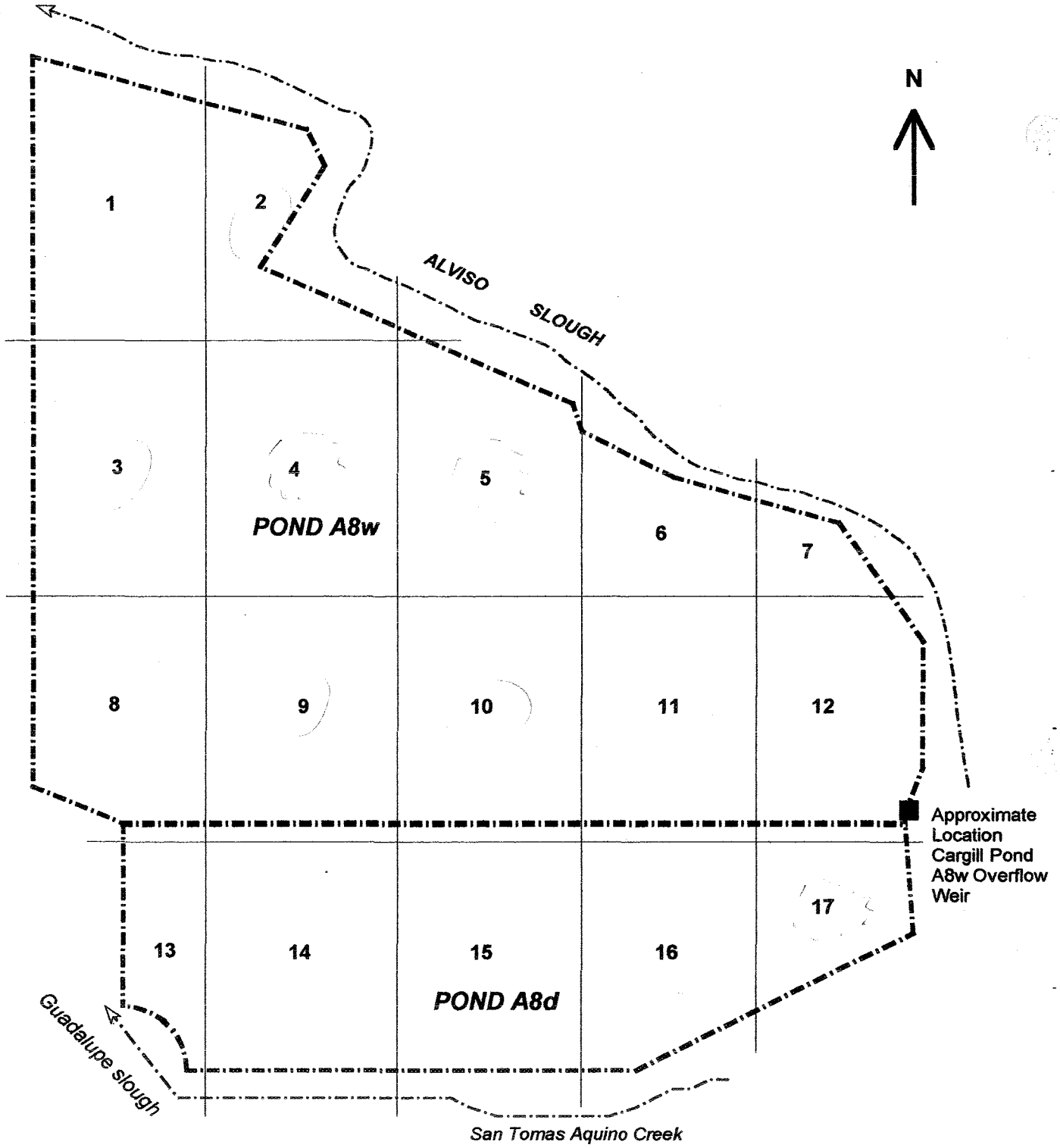
Location Map

Ponds A8W and A8d
Former Cargill Salt Ponds
Don Edwards National Wildlife Refuge
Alviso, CA

Proj. No. 0398
Scale: 1" ≈ 2000'
Date: Mar. 2004

Figure 1

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San Jose, CA



Pond boundary and/or dike and/or levee road.

3 - Sampling grid area number.
One soil sample collected within each grid.

Notes: Pond boundaries shown roughly corespond to shoreline or levee roads separating ponds.
All boundaries are approximate.
Base: Figure 1, Habitat Map, Jones and Stokes, undated.
Sediment samples will be collected near the center of each grid depending upon access and wildlife habitat restrictions.

Sample Location Map

Ponds A8w and A8d
Former Cargill Salt Ponds
Don Edwards National Wildlife Refuge
Alviso, CA

Proj. No. 039
Scale: 1" ≈ 850
Date: Mar. 2004

Figure 2

Light, Air and Space Construction
San Jose, CA

APPENDIX 2

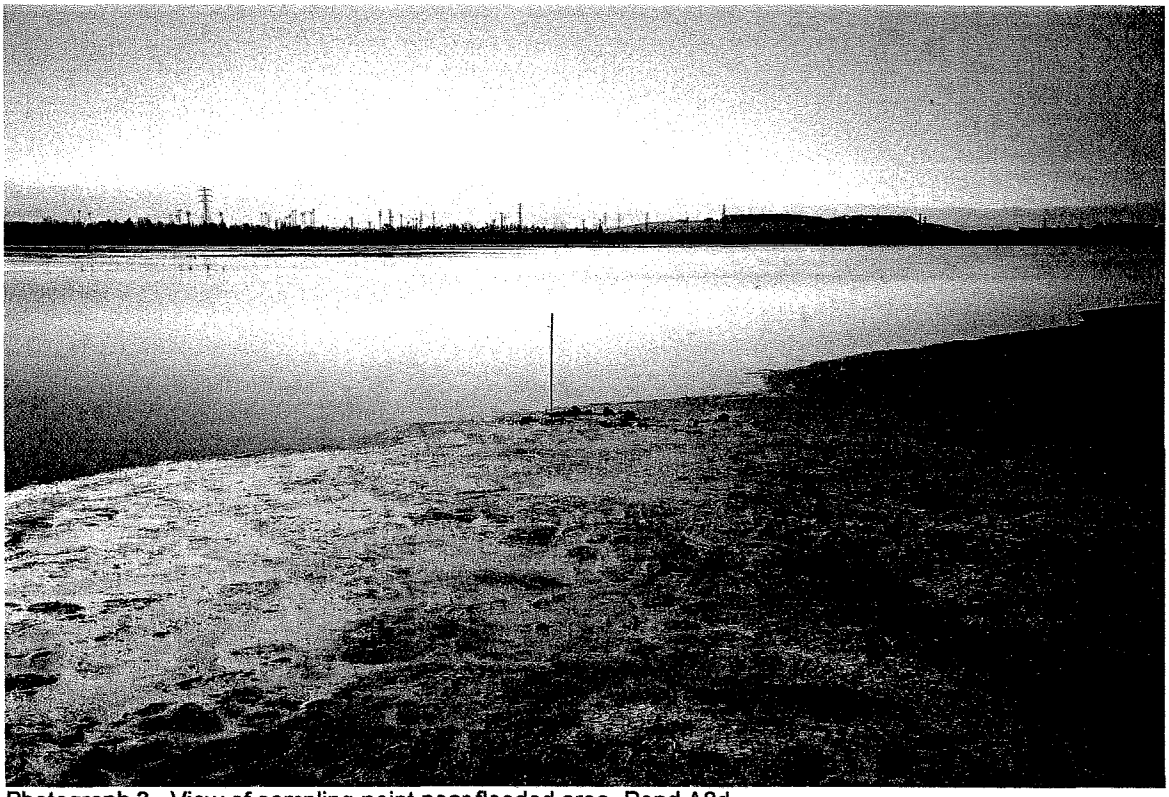
Site Photographs



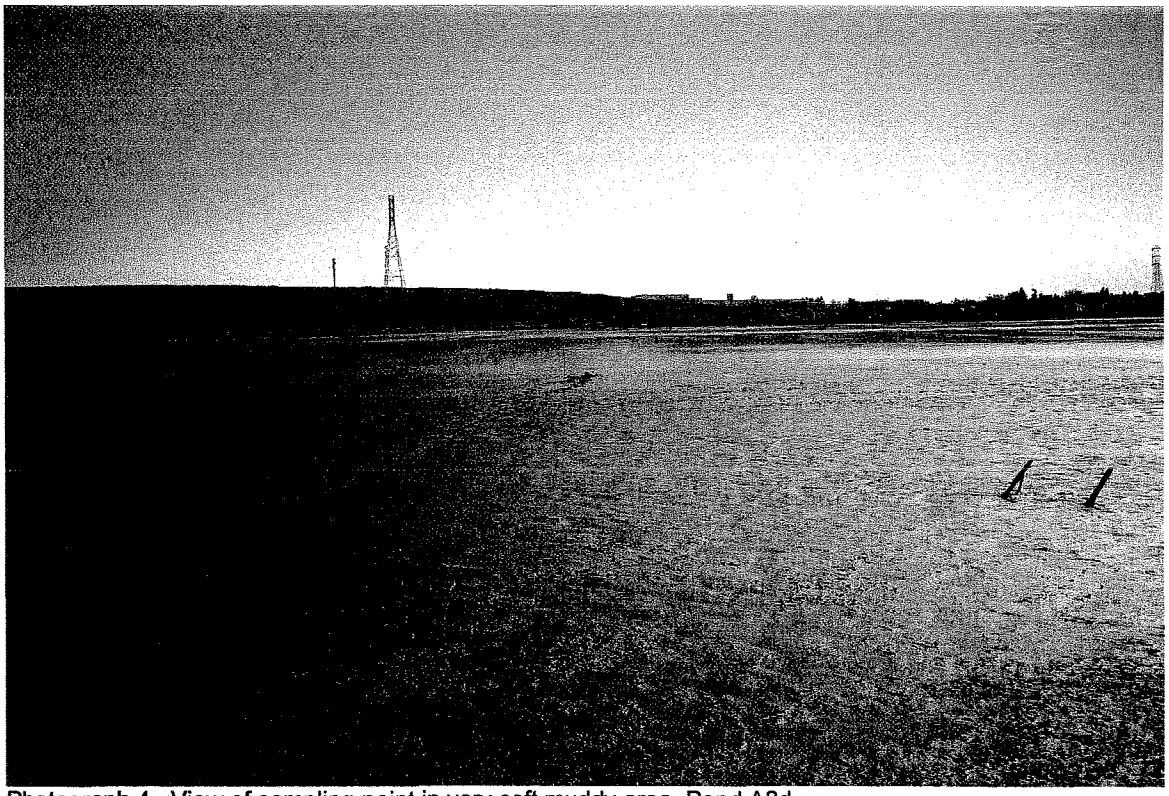
Photograph 1. View of A8w Pond looking to northwest.



Photograph 2. View of sampling from inflatable boat, Pond A8w.



Photograph 3. View of sampling point near flooded area, Pond A8d.



Photograph 4. View of sampling point in very soft muddy area, Pond A8d.

APPENDIX 3

U. S. Fish and Wildlife Conditional Use Permit Information

UNITED STATES DEPARTMENT OF THE INTERIOR
FISH AND WILDLIFE SERVICE

Don Edwards San Francisco Bay
National Wildlife Refuge
PO Box 524, Newark, CA 94560
510/792-0222

SPECIAL USE PERMIT

Station No. to be Credited Permit No.
11640 - 2003-052

Date December 2, 2003

Period of Use (Inclusive)
From December 5, 2003
To January 4, 2004

Permittee Name
David Guthridge 408/979-0661
fax: 408/979-0621

BTA REST (510) 377-5885

Permittee Address
Light, Air & Space Construction
4340 Almaden Expressway, Suite 222
San Jose, CA 95118

Purpose (specify in detail privilege requested, or units of products involved)

Sample Pond A-8 sediment for background mercury concentrations. Permittee will follow November 5, 2003 study proposal titled "Request for Access Permit to Don Edwards National Wildlife Refuge Former Cargill Ponds A8W and A8D on behalf of the Santa Clara Valley Water District".

Description (specify unit numbers: metes and bounds, or other recognizable designations)

Access to Pond A-8 levees and ponds to collect sediment samples using trucks and small boats.

Amount of fee $0 if not a fixed payment, specify rate and unit of charge:

- ☒ Payment Exempt - Justification: Survey beneficial to Refuge
- ☐ Full Payment
- ☐ Partial Payment - Balance of payments to be made as follows:

Record of Payments
N/A

Special Conditions
See attached sheet.

This permit is issued by the U.S. Fish and Wildlife Service and accepted by the undersigned, subject to the terms, covenants, obligations, and reservations, expressed or implied herein, and to the conditions and requirements appearing on the reverse side.

Permittee Signature
David B Guthridge

Issuing Officer Signature and Title
Refuge Manager
Clyde Morris

Form 3-1383 (Rev. 5/97)

LIGHT, AIR & SPACE CONSTRUCTION

ENVIRONMENTAL SERVICES COMPANY
State Contractor's License Number 445403
State EPA R.E.A. Number 04072
Office 408-979-0661

November 4, 2003
LA&S Project No. 0398

U. S. Fish and Wildlife Service
P. O. Box 524
Newark, California 94560

Attn.: Mr. Clyde Morris

Re: Request for Access Permit to Don Edwards National Wildlife Refuge
Former Cargill Salt Ponds A8W and A8D for
Santa Clara Valley Water District Mercury Sediment Background Sampling
Lower Guadalupe River Flood Protection Project, Alviso, CA

Dear Mr. Morris,

Light Air and Space Construction (LA&S) has prepared this Request for Access to Former Cargill Ponds A8W and A8D on behalf of the Santa Clara Valley Water District (SCVWD) for the above referenced site. The proposed work is being performed to sample pond sediment for background mercury concentrations for the Lower Guadalupe River Flood Protection Project Mitigation and Monitoring Plan.

If you have any questions, please call.

Sincerely,
Light, Air and Space Construction

David B. Guthridge
Principal

Christopher M. Palmer
CHG 246; CEG 1262

Attachments: Figure 1. Site Location Map
Figure 2. Proposed Sampling Locations

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1.0 Introduction and Request for Permit to Access Former Cargill Ponds A8w, A8d

The U. S. Fish and Wildlife Service (FWS) requires an approved-use permit to access the Don Edwards Wildlife Refuge (Refuge). Access to some pond areas is restricted due to presence of endangered species and nesting birds. This FWS permit request outlines the reason for entry to sample, the anticipated locations, and sampling procedures together with the anticipated equipment to be used (including boats and boat motors, and any other vehicles and personnel entering the Refuge.

2.0 Background and Technical Approach for Sampling Ponds

The SCVWD has been tasked with developing and implementing a mercury monitoring plan in consultation with the San Francisco Bay Regional Water Quality Control Board (RWQCB) to monitor floodwaters and suspended sediments that could enter the ponds. The purpose of the plan is to determine the concentration of mercury in lower Guadalupe River floodwaters to determine whether they exceed the TMDL objective concentration. The information would then be used to determine whether corrective actions are needed in Cargill Ponds (A8w, A5, A6, A7 or A8d, area roughly bounded by the Alviso Slough and Guadalupe Slough) to reduce mercury concentrations. There has apparently never been a previous mercury soil-sampling program in the ponds or at the weir. This FWS permit request is specifically for the proposed sediment-sampling plan for Ponds A8w and A8d.

The FWS rigorously controls access to all salt ponds areas since the site is located within the Refuge. Santa Clara Valley Water District (SCVWD) gate keys allow initial entrance, but FWS Refuge keys are needed to access the old salt pond levee roads. The access roads and paths are limited, so both overland traversing (where feasible and safe) and sampling from a boat in the ponds will be necessary. Light, Air and Space Environmental Services Company (LA&S) has briefly discussed the site access and initial approach to site sampling with FWS representative Mr. Clyde Morris. Access to some pond areas is restricted due to presence of endangered species and nesting birds.

A safety plan will be prepared for the sampling. The sampling plan will outline the work, type of work and safety gear needed and anticipated sampling conditions. The team members will need to have access and a small working area and a temporary job shack at the entrance of the ponds, located in an approved area by the SCVWD and Refuge FWS. A representative of the Cargill Salt Company was contacted regarding movement around and in the ponds. The Cargill representative informed LA&S that movement on foot on the "dry" pond floors was potentially dangerous due to thin and unstable crusts through which one may sink. It was strongly recommended to LA&S that sampling from a flat-bottom boat was preferable. The Cargill

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representative indicated they would assist LA&S with information on flooding pond depths, depth of water and traversing pond conditions.

2.1 Sampling Rationale

RWQCB states that short term monitoring will include annual site inspections during years one to five following the project construction. The overall approach to monitoring of accumulation of mercury in sediments in Cargill Salt Ponds during the short-term monitoring period will include:

- Collection of background mercury concentration data in salt pond sediments.
- Collecting background mercury concentrations in large flows in the Guadalupe River.
- Collecting water and sediment concentration data and depth of accumulation data if a flood occurs that is large enough to flow into Cargill Ponds.

The purpose of this work plan is to collect initial background chemical data sediment samples at the weir entrance to the ponds and in the ponds (the total pond areas encompass approximately 4,800 acres, Ponds A8w and A8d are estimated at about 1,800 acres). The samples would be collected to ascertain presence and mercury concentrations. It is our understanding that there has not been previous sediment sampling for contaminants in these ponds (see attached Figure 1, Proposed Sample Location Map). Samples would be collected using a random stratified sampling grid since there has not been previous mercury sampling. This type of sampling grid may be used to estimate trends of patterns of contaminants and the approach is to acquire initial data on the presence of mercury in the shallow sediment in the ponds. Each pond is subdivided into approximately equal areas and a sample would be collected as near to the center of the individual grid as possible. Since this area is currently partially flooded and may receive additional water in the future, most sampling is anticipated to be from boats. Some areas of the ponds appear "dry" however surface transit can be treacherous and some "dry" areas may not be accessible safely.

The pond areas are flat and detailed maps are not available for this area. Sample locations will be in areas of dry pond floors, muddy and swampy areas and flooded ponds. Locations of sample points will be recorded by handheld Global Positioning Satellite system that usually yields a location within a three square-meter accuracy. In this way the sample point location can be recorded for return to the same point. Flags and stakes may also be used to mark locations or features of interest observed in the field.

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2.2 Field Methods –Sediment Sampling

Sediment samples will be collected from the locations using either hand coring or sampling from a boat in the flooded areas. Shallow soil borings (about six to 12 inches deep) will be advanced at approximately the locations shown on Figure 2. The shallow boreholes will be drilled with hand coring drilling equipment. All drilling equipment and sampling tools will be cleaned prior to arriving, and before leaving the site. The sampler will then be retrieved and dissembled, and the soil filled acetate or 2x6 inch brass liner will be sealed with Teflon paper or foil and plastic endcaps, labeled, logged onto chain-of-custody forms and place in a chilled ice chest. Soil sample intervals retained for chemical analysis will be cut from the liners at depths of interest. Sediment soil samples may (depending upon field conditions) be collected from a boat may use a conductor through which a drive split spoon sampler would be inserted. Water would be pumped out of the tube, the sampler would be inserted and the soil sample driven.

At the time of work plan preparation, the depth of water in the ponds is unknown, but appears to vary from several inches to several feet depth depending upon the location. Several "canals" exist along the pond access roads and water depth in these is assumed to be at least several feet deep. Water may be cycled through the area by Cargill and the Cargill representative will assist LA&S with information on water depth in ponds.

Field data will be collected on field sheets to document the sampling location. The shallow boreholes will be logged using the Unified Soil Classification System under the supervision of a registered geologist. When sampling in flooded ponds field water measurements will be collected at the sampling location. Water measurements would include pH, dissolved oxygen, oxidation-reduction potential, salinity, temperature and conductivity. Additional lithologic and descriptive information will be collected to describe the sediment at each sample location. The shallow soil borings will collect soil samples at depths of about six inches. Each sample will be labeled, logged onto a chain-of-custody form, and placed in an ice chest on crushed ice for transport to the laboratory. Samples would be sent to the analytical laboratory at the end of each sampling day.

3.0 Summary of Sampling Access and Locations for FWS Access Permit

LA&S will need to be able to move around the perimeter and bottom of Ponds A8D and A8W to collect the required samples. The sample locations are initially plotted on a sketch map, however some locations may need adjustment for access depending upon the ability to move on "dry" pond bottoms and/or depth of water for boating to the required location. LA&S's Refuge access requests for this work and FWS permit are as follows:

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- Up to 17 sampling locations are currently proposed to collect the initial sediment data as shown on Figure 2.
- LA&S will enter the Refuge in the morning of each sampling day and leave the Refuge each night. Gates will be locked following entry or exit to the Refuge.
- Some flags and stakes may be used to assist in sample location marking; no marking paints will be used.
- LA&S plans to move equipment in using medium duty pickup trucks only on the existing access roads. No "off-road" driving is planned on the site. Sampling is anticipated to occur on foot along the pond shore perimeter or from small boats using oars or small motors (if motors are allowed by FWS) for moving on the ponds.
- LA&S will attempt to collect samples from along the pond shore on foot and in the pond bottom by boat however some sampling stations may be deleted if these areas cannot be accessed or sampled safely.
- LA&S anticipates that up to about two weeks may be needed to collect the samples depending upon weather conditions, water depth in ponds and sampling logistics.
- LA&S requests that FWS designate any sensitive areas that should not be entered or avoided by LA&S for this work.
- If an unforeseen problem arise or additional time is needed to finish the work, LA&S will contact the FWS representative if the work extends beyond the approved time constraint of the Refuge access permit.
- LA&S's SCVWD contact is Mr. Terry Newdorf (ph. 408/265-2607 x2695) for this work.

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APPENDIX 4

Chemical Analytical Reports and Chain-of-Custody and
Sample Analytical Methods and QC Documents

Sequoia
Analytical

885 Jarvis Drive
Morgan Hill, CA 95037
(408) 776-9600
FAX (408) 782-6308
www.sequoialabs.com

26 February, 2004

Dave Guthridge
Light Air and Space Construction
P O Box 36303
San Jose, CA 95158

RE: Salt Pond A8D & A8W
Work Order: MNB0400

Enclosed are the results of analyses for samples received by the laboratory on 02/11/04 18:50. If you have any questions concerning this report, please feel free to contact me.

Sincerely,

James Hartley
Project Manager

CA ELAP Certificate #1210

Sequoia Analytical

885 Jarvis Drive
Morgan Hill, CA 95037
(408) 776-9600
FAX (408) 782-6308
www.sequoialabs.com

Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

ANALYTICAL REPORT FOR SAMPLES

Sample ID	Laboratory ID	Matrix	Date Sampled	Date Received
A8W-1	MNB0400-01	Soil	02/11/04 14:23	02/11/04 18:50
A8W-2	MNB0400-02	Soil	02/11/04 14:05	02/11/04 18:50
A8W-3	MNB0400-03	Soil	02/11/04 13:48	02/11/04 18:50
A8W-4	MNB0400-04	Soil	02/11/04 13:33	02/11/04 18:50
A8W-5	MNB0400-05	Soil	02/11/04 13:10	02/11/04 18:50
A8W-6	MNB0400-06	Soil	02/11/04 12:48	02/11/04 18:50
A8W-7	MNB0400-07	Soil	02/11/04 12:25	02/11/04 18:50
A8W-8	MNB0400-08	Soil	02/11/04 14:30	02/11/04 18:50
A8W-9	MNB0400-09	Soil	02/11/04 14:35	02/11/04 18:50
A8W-10	MNB0400-10	Soil	02/11/04 14:41	02/11/04 18:50
A8W-11	MNB0400-11	Soil	02/11/04 14:54	02/11/04 18:50
A8W-12	MNB0400-12	Soil	02/11/04 15:09	02/11/04 18:50
A8W-18	MNB0400-13	Soil	02/11/04 16:15	02/11/04 18:50
A8d-13	MNB0400-14	Soil	02/11/04 13:30	02/11/04 18:50
A8d-14	MNB0400-15	Soil	02/11/04 13:40	02/11/04 18:50
A8d-15	MNB0400-16	Soil	02/11/04 13:05	02/11/04 18:50
A8d-16	MNB0400-17	Soil	02/11/04 12:55	02/11/04 18:50
A8d-17	MNB0400-18	Soil	02/11/04 12:45	02/11/04 18:50
A8d-19	MNB0400-19	Soil	02/11/04 14:20	02/11/04 18:50

The results in this report apply to the samples analyzed in accordance with the chain of custody document. Unless otherwise stated, results are reported on a wet weight basis. This analytical report must be reproduced in its entirety.

Sequoia Analytical

885 Jarvis Drive
Morgan Hill, CA 95037
(408) 776-9600
FAX (408) 782-6308
www.sequoialabs.com

Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Total Metals by EPA 6000/7000 Series Methods

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-1 (MNB0400-01) Soil	**Sampled: 02/11/04 14:23**	**Received: 02/11/04 18:50**							
Mercury	**0.40**	0.0050	mg/kg	1	4B17022	02/17/04	02/17/04	EPA 7471A	
A8W-2 (MNB0400-02) Soil	**Sampled: 02/11/04 14:05**	**Received: 02/11/04 18:50**							
Mercury	**1.1**	0.010	mg/kg	2	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-3 (MNB0400-03) Soil	**Sampled: 02/11/04 13:48**	**Received: 02/11/04 18:50**							
Mercury	**1.3**	0.010	mg/kg	2	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-4 (MNB0400-04) Soil	**Sampled: 02/11/04 13:33**	**Received: 02/11/04 18:50**							
Mercury	**0.67**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-5 (MNB0400-05) Soil	**Sampled: 02/11/04 13:10**	**Received: 02/11/04 18:50**							
Mercury	**0.86**	0.010	mg/kg	2	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-6 (MNB0400-06) Soil	**Sampled: 02/11/04 12:48**	**Received: 02/11/04 18:50**							
Mercury	**0.10**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-7 (MNB0400-07) Soil	**Sampled: 02/11/04 12:25**	**Received: 02/11/04 18:50**							
Mercury	**0.17**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-8 (MNB0400-08) Soil	**Sampled: 02/11/04 14:30**	**Received: 02/11/04 18:50**							
Mercury	**0.12**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-9 (MNB0400-09) Soil	**Sampled: 02/11/04 14:35**	**Received: 02/11/04 18:50**							
Mercury	**1.1**	0.010	mg/kg	2	4B20003	02/20/04	02/20/04	EPA 7471A	

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Sequoia Analytical

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Total Metals by EPA 6000/7000 Series Methods

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-10 (MNB0400-10) Soil	**Sampled: 02/11/04 14:41**	**Received: 02/11/04 18:50**							
Mercury	**1.7**	0.015	mg/kg	3	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-11 (MNB0400-11) Soil	**Sampled: 02/11/04 14:54**	**Received: 02/11/04 18:50**							
Mercury	**0.36**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-12 (MNB0400-12) Soil	**Sampled: 02/11/04 15:09**	**Received: 02/11/04 18:50**							
Mercury	**0.18**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8W-18 (MNB0400-13) Soil	**Sampled: 02/11/04 16:15**	**Received: 02/11/04 18:50**							
Mercury	ND	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8d-13 (MNB0400-14) Soil	**Sampled: 02/11/04 13:30**	**Received: 02/11/04 18:50**							
Mercury	**0.069**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8d-14 (MNB0400-15) Soil	**Sampled: 02/11/04 13:40**	**Received: 02/11/04 18:50**							
Mercury	**0.043**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8d-15 (MNB0400-16) Soil	**Sampled: 02/11/04 13:05**	**Received: 02/11/04 18:50**							
Mercury	**0.082**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8d-16 (MNB0400-17) Soil	**Sampled: 02/11/04 12:55**	**Received: 02/11/04 18:50**							
Mercury	**0.36**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	
A8d-17 (MNB0400-18) Soil	**Sampled: 02/11/04 12:45**	**Received: 02/11/04 18:50**							
Mercury	**0.72**	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Total Metals by EPA 6000/7000 Series Methods

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8d-19 (MNB0400-19) Soil Sampled: 02/11/04 14:20 Received: 02/11/04 18:50									
Mercury	ND	0.0050	mg/kg	1	4B20003	02/20/04	02/20/04	EPA 7471A	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-1 (MNB0400-01) Soil	**Sampled: 02/11/04 14:23**	**Received: 02/11/04 18:50**							
pH	**8.18**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-2 (MNB0400-02) Soil	**Sampled: 02/11/04 14:05**	**Received: 02/11/04 18:50**							
pH	**8.28**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-3 (MNB0400-03) Soil	**Sampled: 02/11/04 13:48**	**Received: 02/11/04 18:50**							
pH	**7.42**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-4 (MNB0400-04) Soil	**Sampled: 02/11/04 13:33**	**Received: 02/11/04 18:50**							
pH	**8.03**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-5 (MNB0400-05) Soil	**Sampled: 02/11/04 13:10**	**Received: 02/11/04 18:50**							
pH	**7.97**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-6 (MNB0400-06) Soil	**Sampled: 02/11/04 12:48**	**Received: 02/11/04 18:50**							
pH	**8.05**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-7 (MNB0400-07) Soil	**Sampled: 02/11/04 12:25**	**Received: 02/11/04 18:50**							
pH	**8.01**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-8 (MNB0400-08) Soil	**Sampled: 02/11/04 14:30**	**Received: 02/11/04 18:50**							
pH	**8.23**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-9 (MNB0400-09) Soil	**Sampled: 02/11/04 14:35**	**Received: 02/11/04 18:50**							
pH	**7.90**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-10 (MNB0400-10) Soil	**Sampled: 02/11/04 14:41**	**Received: 02/11/04 18:50**							
pH	**8.06**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-11 (MNB0400-11) Soil	**Sampled: 02/11/04 14:54**	**Received: 02/11/04 18:50**							
pH	**8.44**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-12 (MNB0400-12) Soil	**Sampled: 02/11/04 15:09**	**Received: 02/11/04 18:50**							
pH	**8.05**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8W-18 (MNB0400-13) Soil	**Sampled: 02/11/04 16:15**	**Received: 02/11/04 18:50**							
pH	**5.44**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8d-13 (MNB0400-14) Soil	**Sampled: 02/11/04 13:30**	**Received: 02/11/04 18:50**							
pH	**6.72**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8d-14 (MNB0400-15) Soil	**Sampled: 02/11/04 13:40**	**Received: 02/11/04 18:50**							
pH	**6.80**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8d-15 (MNB0400-16) Soil	**Sampled: 02/11/04 13:05**	**Received: 02/11/04 18:50**							
pH	**6.88**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8d-16 (MNB0400-17) Soil	**Sampled: 02/11/04 12:55**	**Received: 02/11/04 18:50**							
pH	**6.81**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	
A8d-17 (MNB0400-18) Soil	**Sampled: 02/11/04 12:45**	**Received: 02/11/04 18:50**							
pH	**7.29**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8d-19 (MNB0400-19) Soil Sampled: 02/11/04 14:20 Received: 02/11/04 18:50									
pH	**7.45**	2.00	pH Units	1	4B20011	02/13/04	02/13/04	EPA 9045C	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Anions by EPA Method 300.0

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-1 (MNB0400-01) Soil	**Sampled: 02/11/04 14:23**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1600**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-2 (MNB0400-02) Soil	**Sampled: 02/11/04 14:05**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1200**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-3 (MNB0400-03) Soil	**Sampled: 02/11/04 13:48**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1800**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-4 (MNB0400-04) Soil	**Sampled: 02/11/04 13:33**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**2000**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-5 (MNB0400-05) Soil	**Sampled: 02/11/04 13:10**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**2000**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-6 (MNB0400-06) Soil	**Sampled: 02/11/04 12:48**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1000**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-7 (MNB0400-07) Soil	**Sampled: 02/11/04 12:25**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1600**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-8 (MNB0400-08) Soil	**Sampled: 02/11/04 14:30**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**890**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-9 (MNB0400-09) Soil	**Sampled: 02/11/04 14:35**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1700**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Anions by EPA Method 300.0

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-10 (MNB0400-10) Soil	**Sampled: 02/11/04 14:41**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**2300**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-11 (MNB0400-11) Soil	**Sampled: 02/11/04 14:54**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1700**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-12 (MNB0400-12) Soil	**Sampled: 02/11/04 15:09**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**2100**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8W-18 (MNB0400-13) Soil	**Sampled: 02/11/04 16:15**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**2500**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8d-13 (MNB0400-14) Soil	**Sampled: 02/11/04 13:30**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**1500**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8d-14 (MNB0400-15) Soil	**Sampled: 02/11/04 13:40**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**8000**	500	mg/kg	100	4B20018	02/13/04	02/19/04	EPA 300.0	
A8d-15 (MNB0400-16) Soil	**Sampled: 02/11/04 13:05**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**4000**	500	mg/kg	100	4B20018	02/13/04	02/19/04	EPA 300.0	
A8d-16 (MNB0400-17) Soil	**Sampled: 02/11/04 12:55**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**2700**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	
A8d-17 (MNB0400-18) Soil	**Sampled: 02/11/04 12:45**	**Received: 02/11/04 18:50**							
Sulfate as SO4	**130**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Anions by EPA Method 300.0

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8d-19 (MNB0400-19) Soil Sampled: 02/11/04 14:20 Received: 02/11/04 18:50									
Sulfate as SO4	**140**	50	mg/kg	10	4B20018	02/13/04	02/19/04	EPA 300.0	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods

Sequoia Analytical - Petaluma

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-1 (MNB0400-01) Soil	**Sampled: 02/11/04 14:23**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**14000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-2 (MNB0400-02) Soil	**Sampled: 02/11/04 14:05**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**16000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-3 (MNB0400-03) Soil	**Sampled: 02/11/04 13:48**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**12000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-4 (MNB0400-04) Soil	**Sampled: 02/11/04 13:33**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**10000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-5 (MNB0400-05) Soil	**Sampled: 02/11/04 13:10**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**13000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-6 (MNB0400-06) Soil	**Sampled: 02/11/04 12:48**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**7400**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-7 (MNB0400-07) Soil	**Sampled: 02/11/04 12:25**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**17000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-8 (MNB0400-08) Soil	**Sampled: 02/11/04 14:30**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**12000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-9 (MNB0400-09) Soil	**Sampled: 02/11/04 14:35**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**20000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods

Sequoia Analytical - Petaluma

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8W-10 (MNB0400-10) Soil	**Sampled: 02/11/04 14:41**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**8800**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-11 (MNB0400-11) Soil	**Sampled: 02/11/04 14:54**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**16000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-12 (MNB0400-12) Soil	**Sampled: 02/11/04 15:09**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**12000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8W-18 (MNB0400-13) Soil	**Sampled: 02/11/04 16:15**	**Received: 02/11/04 18:50**							
Total Organic Carbon	ND	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8d-13 (MNB0400-14) Soil	**Sampled: 02/11/04 13:30**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**3500**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8d-14 (MNB0400-15) Soil	**Sampled: 02/11/04 13:40**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**8800**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8d-15 (MNB0400-16) Soil	**Sampled: 02/11/04 13:05**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**18000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8d-16 (MNB0400-17) Soil	**Sampled: 02/11/04 12:55**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**12000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	
A8d-17 (MNB0400-18) Soil	**Sampled: 02/11/04 12:45**	**Received: 02/11/04 18:50**							
Total Organic Carbon	**13000**	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	

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Sequoia Analytical

885 Jarvis Drive
Morgan Hill, CA 95037
(408) 776-9600
FAX (408) 782-6308
www.sequoialabs.com

Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods

Sequoia Analytical - Petaluma

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
A8d-19 (MNB0400-19) Soil Sampled: 02/11/04 14:20 Received: 02/11/04 18:50									
Total Organic Carbon	ND	1000	mg/kg	1	4020487	02/20/04	02/20/04	Walkley Black	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Total Metals by EPA 6000/7000 Series Methods - Quality Control

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes
Batch 4B17022 - EPA 7471A										
Blank (4B17022-BLK1)				Prepared & Analyzed: 02/17/04						
Mercury	0.000140	0.000060	mg/kg							QB-01
Laboratory Control Sample (4B17022-BS1)				Prepared & Analyzed: 02/17/04						
Mercury	0.00741	0.000060	mg/kg	0.00800		92.6	86-113			
Matrix Spike (4B17022-MS1)	**Source: MNB0400-01**			Prepared & Analyzed: 02/17/04						
Mercury	0.780	0.010	mg/kg	0.667	0.40	57.0	86-113			QM-07
Matrix Spike Dup (4B17022-MSD1)	**Source: MNB0400-01**			Prepared & Analyzed: 02/17/04						
Mercury	0.935	0.010	mg/kg	0.667	0.40	80.2	86-113	18.1	10	QM-07
Batch 4B20003 - EPA 7471A										
Blank (4B20003-BLK1)				Prepared & Analyzed: 02/20/04						
Mercury	ND	0.000060	mg/kg							
Laboratory Control Sample (4B20003-BS1)				Prepared & Analyzed: 02/20/04						
Mercury	0.00795	0.000060	mg/kg	0.00800		99.4	86-113			
Matrix Spike (4B20003-MS1)	**Source: MNB0400-02**			Prepared & Analyzed: 02/20/04						
Mercury	1.36	0.010	mg/kg	0.667	1.1	39.0	86-113			QM-07
Matrix Spike Dup (4B20003-MSD1)	**Source: MNB0400-02**			Prepared & Analyzed: 02/20/04						
Mercury	1.33	0.010	mg/kg	0.667	1.1	34.5	86-113	2.23	10	QM-07

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods - Quality Control

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes
Batch 4B20011 - General Preparation										
Duplicate (4B20011-DUP1)	**Source: MNB0400-03**			Prepared & Analyzed: 02/13/04						
pH	7.18	2.00	pH Units		7.42			3.29	20	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Anions by EPA Method 300.0 - Quality Control

Sequoia Analytical - Morgan Hill

Analyte	Result	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes
Batch 4B20018 - General Preparation										
Blank (4B20018-BLK1)				Prepared: 02/13/04	Analyzed: 02/19/04					
Sulfate as SO4	ND	5.0	mg/kg							
Laboratory Control Sample (4B20018-BS1)				Prepared: 02/13/04	Analyzed: 02/19/04					
Sulfate as SO4	96.2	5.0	mg/kg	100		96.2	90-110			
Matrix Spike (4B20018-MS1)	**Source: MNB0400-01**			Prepared: 02/13/04	Analyzed: 02/19/04					
Sulfate as SO4	2750	50	mg/kg	1000	1600	115	80-120			
Matrix Spike Dup (4B20018-MSD1)	**Source: MNB0400-01**			Prepared: 02/13/04	Analyzed: 02/19/04					
Sulfate as SO4	2740	50	mg/kg	1000	1600	114	80-120	0.364	20	

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Conventional Chemistry Parameters by APHA/EPA Methods - Quality Control

Sequoia Analytical - Petaluma

Analyte	Result	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes
Batch 4020487 - General Preparation										
Blank (4020487-BLK1)				Prepared & Analyzed: 02/20/04						
Total Organic Carbon	ND	1000	mg/kg							
Laboratory Control Sample (4020487-BS1)				Prepared & Analyzed: 02/20/04						
Total Organic Carbon	4090	1000	mg/kg	5000		82	80-120			
Matrix Spike (4020487-MS1)	**Source: MNB0400-01**			Prepared & Analyzed: 02/20/04						
Total Organic Carbon	13500	1000	mg/kg	5000	14000	-10	75-125			QM-07
Matrix Spike Dup (4020487-MSD1)	**Source: MNB0400-01**			Prepared & Analyzed: 02/20/04						
Total Organic Carbon	14200	1000	mg/kg	5000	14000	4	75-125	5	35	QM-07

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Light Air and Space Construction	Project: Salt Pond A8D & A8W	MNB0400
P O Box 36303	Project Number: 0398	**Reported:**
San Jose CA, 95158	Project Manager: Dave Guthridge	02/26/04 17:09

Notes and Definitions

QB-01	The method blank contains this analyte at a concentration above the reporting limit; however, the concentration is less than 5% of the sample result, which is negligible according to method criteria.
QM-07	The spike recovery was outside control limits for the MS and/or MSD. The batch was accepted based on acceptable LCS recovery.
DET	Analyte DETECTED
ND	Analyte NOT DETECTED at or above the reporting limit
NR	Not Reported
dry	Sample results reported on a dry weight basis
RPD	Relative Percent Difference

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Light, Air & Space Construction and Environmental Services Company

MNB0400

P.O. Box 36303
San Jose, CA 95158-6303
408-979-0661 office
408-979-0821 fax

4340 Almaden Expressway, Suite 222
San Jose, CA 95118
Contractor's License # 445403, A/B/Hazmat/Well Drilling
REA # 03072

0398
LA&S Project Number

Sand Ranch ABD ABW
LA&S Project Name

Chain of Custody

Date 2-11-04 Page 1 of 3

Sampler's signature

Relinquished by	Relinquished by	Special Instructions
Print Name: David Gabbard Date	Print Name: Date	5-day
Signature: Time	Signature: Time	
Company Name: LA&S	Company Name:	
Received By	Received By	
Print Name: Date	Print Name: Date	
Signature: Time	Signature: Time	
Company Name:	Company Name:	
9		
# of Containers	Preserved (Yes/No)	Chain of Custody Seals	Conforms to Record

Sample I.D.	Date	Time	Matrix	Lab I.D.	Analysis Requested: TPH as Gas BTEX MTBE	TPH Diesel	Sulfate	pH	Total Organic Carbon	Total Mercury	Monomethyl Mercury						Number of Containers
ABW-1	2/11/04	1423	S	MNB0400-01			✓	✓	✓	✓	✓						1
ABW-2	2/11/04	1405	S	-02			✓	✓	✓	✓	✓						1
ABW-3	2/11/04	1348	S	-03			✓	✓	✓	✓	✓						1
ABW-4	2/11/04	1333	S	-04			✓	✓	✓	✓	✓						1
ABW-5	2/11/04	1310	S	-05			✓	✓	✓	✓	✓						1
ABW-6	2/11/04	1248	S	-06			✓	✓	✓	✓	✓						1
ABW-7	2/11/04	1225	S	-07			✓	✓	✓	✓	✓						1
ABW-8	2/11/04	1430	S	-08			✓	✓	✓	✓	✓						1
ABW-9	2/11/04	1435	S	-09			✓	✓	✓	✓	✓						1

Light, Air & Space Construction and Environmental Services Company

P.O. Box 36303
San Jose, CA 95158-6303
408-929-0661 office
408-979-0621 fax

4340 Almaden Expressway, Suite 222
San Jose, CA 95118
Contractor's License # 445403, A/HazMat/Well Drilling
REA # 04072

MW80400

0398
LA&S Project Number

Salt Flats ABG ABW
LA&S Project Name

Chain of Custody

Date 2-11-04 Page 2 of 3

Sampler's signature

Relinquished by	Relinquished by	Special Instructions
Printed name: David Gilmadge Date: 2/11/04	Printed name: Date:	5day
Signature: Time:	Signature: Time:	
Company Name: LA&S	Company Name:	
Received By	Received By	
Printed name: Date: 2/11/04	Printed name: Date:	
Signature: Time: 1850	Signature: Time:	
Company Name: Seq. MA	Company Name:	

# of containers		Method of Shipment	Conforms to Record
4			

Sample I.D.	Date	Time	Matrix	Lab I.D.	TPH as Gas & BTEX	TPH as Diesel	Sulphate	pH	Total Organic Carbon	Total Mercury	Monomethyl Mercury						Expedited TAT	Expedited TAT	# of containers
ABW-10	2/11/04	1441	S	-10			✓	✓	✓	✓	✓								1
ABW-11	2/11/04	1454	S	-11			✓	✓	✓	✓	✓								1
ABW-12	2/11/04	1509	S	-12			✓	✓	✓	✓	✓								1
ABW-13	2/11/04	1615	S	-13			✓	✓	✓	✓	✓								1

Light, Air & Space Construction and Environmental Services Company

P.O. Box 36303
San Jose, CA 95158-6303
408-979-0801 office
408-979-0821 fax

4340 Almaden Expressway, Suite 222
San Jose, CA 95118
Contractor's License # 445403, A/D/HazMat/Well Drilling
REA # 04972

MW80400

0398
L.A&S Project Number

Sept Navy ABD 4880
L.A&S Project Name

Chain of Custody

Date 2-11-04 Page 3 of 3

Sampler's Signature

Relinquished by: David Guttenberger 2/11/04 1847

Received By: Tung Tien Le 2/11/04 1847 Sky, MA

Special Instructions: 5-day

6

Analysis Requested

Sample I.D	Date	Time	Matrix	Lab I.D.	TRPH EPA 418.1	TRPH Diesel	Sulfate	pH	Total Organic Carbon	Total Mercury	Monomethyl Mercury	Extraction Type	Extraction Type	Number of Containers
ABd-13	2/11/04	1330	S	-14			✓	✓	✓	✓	✓			1
ABd-14	2/11/04	1340	S	-15			✓	✓	✓	✓	✓			1
ABd-15	2/11/04	1305	S	-16			✓	✓	✓	✓	✓			1
ABd-16	2/11/04	1255	S	-17			✓	✓	✓	✓	✓			1
ABd-17	2/11/04	1245	S	-18			✓	✓	✓	✓	✓			1
ABd-19	2/11/04	1420	S	-19			✓	✓	✓	✓	✓			1

BROOKSRAND
TRACE METALS ANALYSIS & PRODUCTS

February 27, 2004

Sequoia Analytical
Attn.: James Hartley
885 Jarvis Drive
Morgan Hill, CA 95037

RE: Brooks Rand Project: SEQ002; Tracking #: 04BR090

Dear Mr. Hartley,

This report is for the monomethyl mercury analysis of nineteen sediment samples collected on 2/11/04 and received at Brooks Rand on 2/18/04. These samples have been assigned the BRL tracking number 04BR090. The samples were received, stored, prepared and analyzed according to Brooks Rand LLC Standard Operating Procedures. Samples were received at 1.0°C and were stored at <-10°C in a locked sample storage freezer until sample preparation.

Monomethyl Mercury Analysis
Sediment samples were prepared by acid bromide/methylene chloride extraction. Samples were analyzed by ethylation, purge and trap, GC column separation, thermal decomposition and atomic fluorescence detection. Samples were analyzed by a modification of EPA draft method 1630, as detailed in the Brooks Rand Method BR-0011. All results have been blank corrected as described in EPA 1630.

Batch 04-111
Samples were prepared 2/25/04 and analyzed on 2/26/04. Refer to the QA Report for QA results. All QA criteria were met. Sample results below the method detection limit (MDL) have been assigned the lab qualifier "U" for non-detect and are reported at the MDL. Results above the detection limit and below the quantitation limit are qualified "B" for estimate. No additional qualification of the data was required.

If there are any questions, please feel free to contact me.

Sincerely,

Elizabeth Madonick

3958 6th Avenue NW • Seattle, WA 98107 • Phone (206) 632-6206 • Fax (206) 632-6017 • www.brooksrand.com • brl@brooksrand.com

Reported by

Brooks Rand LLC

Contact: Colin Davies

3958 6th Avenue NW
Seattle, WA 98107
Tel: 206-632-6206 *Fax: 206-632-6017*

Summary of Results for

Sequoia Analytical

Contact: James Hartley

885 Jarvis Drive
Morgan Hill *CA* *95037*
Tel: 408-782-8166

Lab Project # SEQ002
Lab Tracking # 04BR090

Lab Services Agreement 042302SEQ002

Sample/Sampling/Receiving Info

Sequoia Analytical		*BRL*	
Sample Identification	**Sampling Date**	**Sample Number**	**Receiving Date**
MNB0400	2/11/04	04BR090 - 1	2/18/04
MNB0400	2/11/04	04BR090 - 2	2/18/04
MNB0400	2/11/04	04BR090 - 3	2/18/04
MNB0400	2/11/04	04BR090 - 4	2/18/04
MNB0400	2/11/04	04BR090 - 5	2/18/04
MNB0400	2/11/04	04BR090 - 6	2/18/04
MNB0400	2/11/04	04BR090 - 7	2/18/04
MNB0400	2/11/04	04BR090 - 8	2/18/04
MNB0400	2/11/04	04BR090 - 9	2/18/04
MNB0400	2/11/04	04BR090 - 10	2/18/04
MNB0400	2/11/04	04BR090 - 11	2/18/04
MNB0400	2/11/04	04BR090 - 12	2/18/04
MNB0400	2/11/04	04BR090 - 13	2/18/04
MNB0400	2/11/04	04BR090 - 14	2/18/04
MNB0400	2/11/04	04BR090 - 15	2/18/04
MNB0400	2/11/04	04BR090 - 16	2/18/04
MNB0400	2/11/04	04BR090 - 17	2/18/04
MNB0400	2/11/04	04BR090 - 18	2/18/04
MNB0400	2/11/04	04BR090 - 19	2/18/04

Friday, February 27, 2004

Project Manager

Reported by

Brooks Rand LLC

Contact: Colin Davies

3958 6th Avenue NW
Seattle, WA 98107
Tel: 206-632-6206 Fax: 206-632-6017

Summary of Results for

Sequoia Analytical

Contact: James Hartley

885 Jarvis Drive
Morgan Hill CA 95037
Tel: 408-782-8166

Lab Project # SEQ002
Lab Tracking # 04BR090

Lab Services Agreement 042302SEQ002

Hg(Monomethyl)

Sample Identification	BRL Number	Preparation date	Analysis date	Batch #	Result	Units	Qualifier (Q)
MNB0400	04BR090 - 1	2/25/04	2/26/04	04-111	0.020	ng/g	U
MNB0400	04BR090 - 2	2/25/04	2/26/04	04-111	12.100	ng/g	
MNB0400	04BR090 - 3	2/25/04	2/26/04	04-111	2.600	ng/g	
MNB0400	04BR090 - 4	2/25/04	2/26/04	04-111	0.048	ng/g	B
MNB0400	04BR090 - 5	2/25/04	2/26/04	04-111	0.686	ng/g	
MNB0400	04BR090 - 6	2/25/04	2/26/04	04-111	1.490	ng/g	
MNB0400	04BR090 - 7	2/25/04	2/26/04	04-111	0.020	ng/g	U
MNB0400	04BR090 - 8	2/25/04	2/26/04	04-111	0.031	ng/g	B
MNB0400	04BR090 - 9	2/25/04	2/26/04	04-111	0.317	ng/g	
MNB0400	04BR090 - 10	2/25/04	2/26/04	04-111	1.040	ng/g	
MNB0400	04BR090 - 11	2/25/04	2/26/04	04-111	0.627	ng/g	
MNB0400	04BR090 - 12	2/25/04	2/26/04	04-111	0.054	ng/g	
MNB0400	04BR090 - 13	2/26/04	2/26/04	04-111	0.020	ng/g	U
MNB0400	04BR090 - 14	2/25/04	2/26/04	04-111	0.337	ng/g	
MNB0400	04BR090 - 15	2/25/04	2/26/04	04-111	0.047	ng/g	B
MNB0400	04BR090 - 16	2/25/04	2/26/04	04-111	0.781	ng/g	
MNB0400	04BR090 - 17	2/25/04	2/26/04	04-111	0.174	ng/g	
MNB0400	04BR090 - 18	2/25/04	2/26/04	04-111	0.236	ng/g	
MNB0400	04BR090 - 19	2/25/04	2/26/04	04-111	0.045	ng/g	B

Friday, February 27, 2004

Project Manager

BRL QA Report

Batch #: 04-111 *Method #:* BR-0011

Analyte: MMHg *Matrix:* Sediment

BIAS *Criteria: Recovery = 65-135%*			
Certified Reference Material (CRM)			
CRM ID	*Certified Value ng/g*	*Measured Value ng/g*	*Recovery %*
BCR 580	75.5	63.2	83.7%
BCR 580	75.5	65.5	86.7%

BIAS *Criteria: Recovery = 67-133%*			
Ongoing Precision and Recovery (OPR)			
LCS ID	*Certified Value ng/L*	*Measured Value ng/L*	*Recovery %*
ICV	5.00	5.33	106.6%
OPR1	0.25	0.250	100.1%
OPR2	0.25	0.230	92.1%

BIAS *Criteria: Recovery = 65-135%, RPD<35%*								
Matrix Spikes and Spike Duplicates								
		Matrix Spike			*Matrix Spike Dupicate*			
Sample ID	*Sample Value ng/g (wet)*	*Spiked Value ng/g (wet)*	*Measured Value ng/g (wet)*	*MS Recovery %*	*Spiked Value ng/g (wet)*	*Measured Value ng/g (wet)*	*MSD Recovery %*	*Duplicate RPD*
04BR090-3	2.60	20.2	22.3	97.3%	20.0	22.6	99.8%	1.4%
04BR090-16	0.761	20.3	21.2	100.4%	20.5	21.3	100.4%	0.7%

Method Blanks (MB) *Criteria: Avg. < 2 x MDL and St. Dev. < 2/3rd of MDL*						
MB1	*MB2*	*MB3*	*Average*	*StDev*	*MDL*	*PQL*
ng/g	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
-0.001	0.004	0.004	0.002	0.002	0.02	0.05

2/27/2004

Elizabeth Mcdaniel
Project Manager

Reported by

Brooks Rand LLC

Contact: Elizabeth Madonick

3958 6th Avenue NW
Seattle, WA 98107
Tel: 206-632-6206 Fax: 206-632-6017

Summary of Results for

Sequoia Analytical

Contact: James Hartley

885 Jarvis Drive
Morgan Hill CA 95037
Tel: 408-782-8166

Lab Project # SEQ002
Lab Tracking # 04BR090

Lab Services Agreement 042302SEQ002

Sample/Sampling/Receiving Info

Sequoia Analytical		*BRL*	
Sample Identification	**Sampling Date**	**Sample Number**	**Receiving Date**
A8W-1	2/11/04	04BR090 - 1	2/18/2004
A8W-2	2/11/04	04BR090 - 2	2/18/2004
A8W-3	2/11/04	04BR090 - 3	2/18/2004
A8W-4	2/11/04	04BR090 - 4	2/18/2004
A8W-5	2/11/04	04BR090 - 5	2/18/2004
A8W-6	2/11/04	04BR090 - 6	2/18/2004
A8W-7	2/11/04	04BR090 - 7	2/18/2004
A8W-8	2/11/04	04BR090 - 8	2/18/2004
A8W-9	2/11/04	04BR090 - 9	2/18/2004
A8W-10	2/11/04	04BR090 - 10	2/18/2004
A8W-11	2/11/04	04BR090 - 11	2/18/2004
A8W-12	2/11/04	04BR090 - 12	2/18/2004
A8W-18	2/11/04	04BR090 - 13	2/18/2004
A8W-13	2/11/04	04BR090 - 14	2/18/2004
A8W-14	2/11/04	04BR090 - 15	2/18/2004
A8W-15	2/11/04	04BR090 - 16	2/18/2004
A8W-16	2/11/04	04BR090 - 17	2/18/2004
A8W-17	2/11/04	04BR090 - 18	2/18/2004
A8W-19	2/11/04	04BR090 - 19	2/18/2004

Tuesday, March 16, 2004

Project Manager

Reported by

Brooks Rand LLC

Contact: Elizabeth Madonick

3958 6th Avenue NW
Seattle, WA 98107
Tel: 206-632-6206 Fax: 206-632-6017

Summary of Results for

Sequoia Analytical

Contact: James Hartley

885 Jarvis Drive
Morgan Hill CA 95037
Tel: 408-782-8166

Lab Project # SEQ002
Lab Tracking # 04BR090

Lab Services Agreement 042302SEQ002

Hg(Monomethyl)

Sample Identification	BRL Number	Preparation date	Analysis date	Batch #	Result	Units	Qualifier (Q)
A8W-1	04BR090 - 1	2/25/2004	2/26/2004	04-111	0.020	ng/g	U
A8W-2	04BR090 - 2	2/25/2004	2/26/2004	04-111	12.100	ng/g	
A8W-3	04BR090 - 3	2/25/2004	2/26/2004	04-111	2.600	ng/g	
A8W-4	04BR090 - 4	2/25/2004	2/26/2004	04-111	0.048	ng/g	B
A8W-5	04BR090 - 5	2/25/2004	2/26/2004	04-111	0.688	ng/g	
A8W-6	04BR090 - 6	2/25/2004	2/26/2004	04-111	1.490	ng/g	
A8W-7	04BR090 - 7	2/25/2004	2/26/2004	04-111	0.020	ng/g	U
A8W-8	04BR090 - 8	2/25/2004	2/26/2004	04-111	0.031	ng/g	B
A8W-9	04BR090 - 9	2/25/2004	2/26/2004	04-111	0.317	ng/g	
A8W-10	04BR090 - 10	2/25/2004	2/26/2004	04-111	1.040	ng/g	
A8W-11	04BR090 - 11	2/25/2004	2/26/2004	04-111	0.627	ng/g	
A8W-12	04BR090 - 12	2/25/2004	2/26/2004	04-111	0.054	ng/g	
A8W-18	04BR090 - 13	2/25/2004	2/26/2004	04-111	0.020	ng/g	U
A8W-13	04BR090 - 14	2/25/2004	2/26/2004	04-111	0.337	ng/g	
A8W-14	04BR090 - 15	2/25/2004	2/26/2004	04-111	0.047	ng/g	B
A8W-15	04BR090 - 16	2/25/2004	2/26/2004	04-111	0.761	ng/g	
A8W-16	04BR090 - 17	2/25/2004	2/26/2004	04-111	0.174	ng/g	
A8W-17	04BR090 - 18	2/25/2004	2/26/2004	04-111	0.236	ng/g	
A8W-19	04BR090 - 19	2/25/2004	2/26/2004	04-111	0.045	ng/g	B

Tuesday, March 16, 2004

Project Manager

Brooks Rand LLC Sample Receiving Log

Tracking #	**04BR090**
Customer:	Sequoia Analytical
Contact:	James Hartley
Project Ref. #:	SEQ002
Collection Date	2/11/04
QA Level	Standard
Sample Condition	Intact
Shipping container intact?	Yes
Shipping container type:	Cooler
Shipping container temp:	1°C
Shipping container coolant:	Ice
Sample preservation:	N/A
Acid lab #	
Hg Concentration:	
Sample storage area:	BRL Freezer #4
Sample Turnaround Time:	
Contract Turnaround Time:	14 days

Due Date:	3/3/04
Receiving Date:	2/18/04
Receiving Time:	8:30 AM
Logged-in by:	Biniam Zelelow
Log-in Date:	2/18/04
Log-in Time:	11:28 AM
Airbill present?	Yes
Airbill #	1Z 97E 15W 01 40
Carrier:	UPS
Custody seal present?	Yes
Custody seal intact?	Yes
COC Present?	Yes
COC Number:	N/A
Analysis request form?	Yes
COC/Sample tag agree?	Yes

See SOW	No	See Project Manage	No
See Mem	No	See Lab Manage	No
Consult MSDS	No	See Contract Inf	No

Comments:

Lab ID:	Sample Tag #	Container #	Size:	pH	Matrix/Sub-Matrix	Comments:
1	A8W-1	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
2	A8W-2	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
3	A8W-3	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
4	A8W-4	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
5	A8W-5	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
6	A8W-6	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			

Lab ID:	Sample Tag #	Container #	Size:	pH	Matrix/Sub-Matrix	Comments:
7	A8W-7	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
8	A8W-8	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
9	A8W-9	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
10	A8W-10	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
11	A8W-11	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
12	A8W-12	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
13	A8W-18	2 oz. Jar	Glass Jar		Sediment,	sample is sandy.
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
14	A8W-13	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
15	A8W-14	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
16	A8W-15	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
17	A8W-16	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
18	A8W-17	2 oz. Jar	Glass Jar		Sediment,	
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			
19	A8W-19	2 oz. Jar	Glass Jar		Sediment,	Sample is sandy.
Analysis / Method:		Hg(Monomethyl)	EPA 1630 Mod.			

Sample Custodian signature 3/16/04 Date

Confidential

SOP #BR-0011

Determination of Methylmercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection

Brooks Rand, Ltd.

Revision 006
Revised 05/23/00
Written 1/90

Reviewed _____
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_____	_____
President	Date
_____	_____
QA Manager	Date
_____	_____
Senior Scientist	Date
_____	_____
Scientist (if applicable)	Date

Determination of Methylmercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection

1. DESCRIPTION

1.1. Mono-methylmercury (MMHg) is determined by an improved method (Liang, Bloom, and Horvat 1994). The MMHg is first ethylated with sodium tetraethylborate (BEt_4^-) and collected by purging with dry, Hg free Nitrogen onto a column filled with either Carbotrap™ or Tenax. The ethyl mercury derivatives are then thermally desorbed and transferred to a GC column held in an oven at 105° C, which chromatographically separates the species. The organo-Hg compounds are decomposed at 900° C to Hg(0), then quantified by a cold vapor atomic fluorescence spectrophotometer (CVAFS). This method can be applied for the determination of MMHg in a variety of sample matrices and has been demonstrated as being very sensitive, precise, and accurate. Very good results were obtained for the determination of MMHg in standard and certified reference materials and numerous intercalibration samples (Liang, Bloom, and Horvat 1994).

2. APPARATUS AND MATERIAL

2.1. Atomic fluorescence spectrophotometer (BRL part #AF-03): CVAFS systems are built by Brooks Rand, Ltd. (BRL Model III). Refer to the "Brooks Rand, Ltd. Model III Operations Manual" for instrument operating instructions.

2.2. Data Acquisition : Integration software (BRL Mercury Guru Version 2.0 or later) with PC for peak area measurements. Alternatively a chart recorder (Yokogawa 3021) for peak height measurements may be used.

2.3. Reaction and purge vessels (BRL part #AF-32): A 150 mL flat bottom bottle with 24/40 tapered fitting is used as the reaction vessel, in conjunction with a special 4-way valve sparging-tube cap-assembly. This valve assembly allows the water sample to react initially with the ethylating reagent, without bubbling, then to be purged onto the trapping column, and finally to be bypassed, so that water vapor adsorbed onto the column may be evaporated by the direct flow of dry carrier gas.

2.4. Trapping column (BRL part #AF-21): Tenax traps used for the collection of purged organomercury species measuring 10 cm long of 6.4 mm outside diameter x 4.0 mm inside diameter. Figure 1 also shows the connection of the column and a reaction vessel.

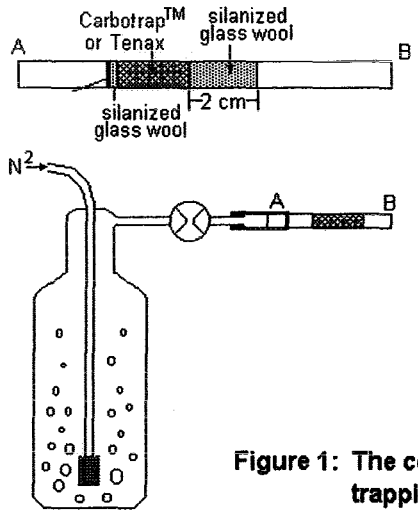


Figure 1: The construction of trapping column and its connection with a reaction vessel

2.5. Guard Column: If a Tenax TA trap is to be used for collecting purged species, a pre-GC column OV-3 trap must also be used. This guard column is placed between the Tenax trap and the GC column and serves to inhibit Tenax material from entering the GC column. The guard column consists of approximately 70 mg of OV-3 3% packed in the same type of quartz tube used for the trapping column, between quartz wool plugs. The guard column is initially conditioned by heating twice for 30 seconds, allowing the trap to cool between heatings. The guard column should be blanked daily with the trapping columns before analysis. Guard columns should be replaced routinely at least every four (4) months or when a problem arises.

2.6. Isothermal gas chromatography system: consisting of GC column (BRL part #AF-34), GC oven (BRL part #AF-33), pyrolitic column (AF-35) and temperature controller for GC oven (BRL part #AF-36). For a diagram of the system see Figure 2. Under a 45 mL/min flow of high purity helium, organomercury species desorbed from a trapping column are carried by gas passing through the GC column, held at 105° C in a cylindrical oven, and eluted. Separated species are decomposed in a thermal decomposition tube and finally detected by CVAFS.

3. REAGENTS, GASES, AND WATER

3.1. MMHg Standard solutions

a) Standard stock solution: 1 mg/mL MMHg, as Hg. Dissolve 0.1252 gram CH_3HgCl (95%+) in a 100 mL class A volumetric flask with isopropanol. Alternatively, a 1mg/mL stock solution may be obtained from a commercial vendor (Alfa Aesar or equivalent). This solution's concentration is verified by analyzing a dilution of a solution that is obtained from an independent source.

b) Intermediate stock solution: 1 µg/mL MMHg. Dilute 0.10 mL of 1 mg/mL stock solution to 100 mL with DDW. This solution expires after one month.

c) Working standard: 1 ng/mL MMHg. Dilute 0.10 mL of 1 µg/mL intermediate stock solution to 100 mL with DDW. This solution expires daily.

d) Working standard: 0.1 ng/mL MMHg. Dilute 1.0 mL of 1 ng/mL stock solution to 10 mL with DDW. This solution expires daily.

3.2. Sodium tetraethylborate ($NaBEt_4$) solution: Dissolve one gram of $NaBEt_4$ (stored in freezer) in 10 mL of 2% KOH solution chilled previously in the refrigerator to produce a 10% stock solution. This solution is stored in the refrigerator and expires after one month. Dilute 0.3 mL of the 10% stock solution to 3.0 mL with the chilled 2% KOH solution to produce a working 1% NaBEt4 solution. This solution is stored in the refrigerator when not in use and expires daily.

3.3. Sodium acetate buffer: A 2M acetate buffer is prepared by dissolving 272 g of reagent grade sodium acetate and 118 mL of glacial acetic acid in DDW to a final volume of 1 L. This solution is purified of trace mercury by the addition of 5 g of 1 N HCl-rinsed sulfhydoxyl chelating resin (Sumitomo Q-10R) to the bottle and agitation. The solution is stored in a Teflon FEP bottle and filtered prior to use.

3.4. Potassium hydroxide methanol solution: Dissolve 250 g of reagent grade KOH pellets in high purity methanol to a final volume of 1 L. The solution is stored in a Teflon FEP bottle.

3.5. Gases: Helium used as a GC carrier gas is ultra high-purity grade and passed through water and oxygen removal traps. Nitrogen used as a purge gas for sweeping derivatives from a bubbler is plumbed from cryogenic bleed-off. Both are passed through a gold-coated sand trap to remove traces of mercury prior to use.

3.6. Water: Double Deionized Water (DDW) from a Millipore System is used throughout.

3.7. 20 % KCl / 0.2 % L-Cysteine solution: Dissolve 20.0 g KCl and 0.2 g L-Cysteine in 100 mL of DDW. This solution should be discarded and replaced every 6 months or if crystals begin to form.

3.8. 9 M H_2SO_4: Mix equal parts DDW and pre-analyzed, concentrated H_2SO_4. Introduce the reagents slowly as this procedure generates a great deal of heat. Allow to cool completely before capping tightly.

3.9. 0.05 % $NH_2OH{\bullet}HCl$: Dilute 200 µL of 30 % $NH_2OH{\bullet}HCl$, used for Total Hg analysis, to 120 mL DDW. Discard and replace after 10 days.

4. ANALYSIS

Standards, typically 0, 10, 50, 100, 250, 1000, 2000 pg for MMHg are added into reaction vessels containing 50-75 mL of DDW and 200 µl of 2M acetate buffer. For samples, add appropriate sample volumes plus DDW as necessary for a final bubbler volume of 50 to 75 mL (for sample preparation see section 6). Some acid can be carried over during distillation: Adjust pH in the bubbler to approximately 6.2 by adding 20% KOH and/or 1:1 HOAc solutions before adding buffer, if needed. (Solution should be clear or yellow in the presence of methyl red indicator.) Subsequent addition of buffer will bring the pH to the optimum range of 3.5-5.5. An aliquot of 50 µl (75 µl for biota samples) of $NaBEt_4$ is added, the 4-way valve-cap inserted and clamped, and the vessel swirled to wash any droplets back into solution. Allow the mixture to react without purging for 15 minutes. Place a trapping column in the orientation shown in Figure 1, and then purge with N_2 at a flow rate of 250 $mL \cdot min^{-1}$ for 12 minutes. The organomercury compounds are swept from solution and collected onto the trapping column. Then the valve is switched to pass dry gas over the column for 5 minutes, to remove water condensation from the trap. Biota samples should be allowed to react without purging for 20 minutes, purged with N_2 for 15 minutes and allowed to dry for 5 minutes. Afterwards, connect the trapping column in-line with the GC column (Fig. 2).

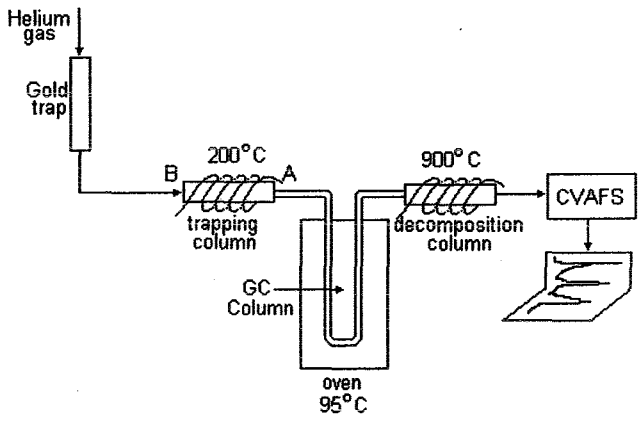


FIGURE 2: A schematic diagram of isothermal gas chromatograph system

When using a carbotrap, special attention must be paid to the orientation of the trap shown in Figure 2. The trap is placed so that the end facing the bubbler output is now facing the GC column input to avoid the organomercury species passing through the entire length of the heating trap column and decomposing to Hg(0) (Liang, Bloom, and Bloom 1994). Under a helium flow rate of 45 mL/minute, apply appropriate voltage to the coil around the column so that the column reaches 200° C from room temperature within 30 seconds. The heating is controlled by switching on a timer connected in-line, while turning on the integrator or chart recorder. The organomercury species are desorbed and carried through the GC column held in an oven at 105° C. The species elute in order of increasing molecular weight, pass through the thermal decomposition tube, held at approximately 900° C at which point all organomercury species are

converted into Hg(0), and detected by CVAFS. The sparging/reaction vessels must be rinsed with DDW after each use, to flush out reaction by-products which can interfere with subsequent purgings.

5. CALCULATIONS

Calculations may be made by reading off the (linear) standard curve, or by the following method, which is functionally the same.

Calculate a mean (B) "peak area or peak height of the calibration (bubbler) blank".
Calculate a mean coefficient (C)

$$C = \frac{pgHg}{PA - B}$$

where PA is the peak area or peak height of the aliquot of standard.

Calculate the concentration of each species in sample by the following formula:

For aqueous samples:

$$ng\ of\ Hg/L = \{[C\cdot(S-B)\cdot V_2/V_1]-MB\}/V_3$$

where S is the peak area or peak height of the sample aliquot, V_1 is the analyzed sample aliquot size in mL, V_2 is the final dilution volume of the distillate in mL, MB is the total picograms of the method blank and V_3 is the original sample volume distilled in mL.

$$MB = C\cdot(S-B)\cdot V_2/V_1$$

where S is the peak area or peak height of method blank in mm, V_1 is the analyzed method blank aliquot size in mL, and V_2 is the final dilution volume of the method blank distillate in mL.

For solid samples:

Solid samples are calculated in the same manner as above except that V_3 is the original sample weight digested or distilled in mg, with the result being in ng/g.

6. SAMPLE PREPARATION

Depending on the purposes and definitions of investigations of mercury biogeochemistry cycling, samples are prepared in the following methods prior to analysis.

6.1. Preparation of aqueous samples for MMHg analysis.

The following two isolation methods, distillation and solvent extraction, have been used in our labs for the determination of MMHg in aqueous samples. Good agreement was obtained in the comparison of the two methods for most water samples studied: for organic rich and/or high level sulfide containing samples, the distillation showed some advantages over the solvent extraction method with higher recoveries (85 ± 4%, Horvat, Bloom, and Liang, 1993). In addition, extraction consumes large quantities of organic solvent which can result in environmental contamination. Therefore, distillation is preferred.

6.1.1. Distillation:

Reagents: 20% KCl in 0.2 % L-Cysteine, 9 M H_2SO_4, 0.05% $NH_2OH{\cdot}HCl$

Distillation devices: Vials and caps for distillation and distillate collection are made of Teflon obtained by Savillex Corporation, USA. Caps have 1/8" ports for friction fit 1/8" Teflon tubing. Instead of Teflon, a glass distillation still may also be used (Horvat and Stoeppler, 1988).

Distillation procedures: An aliquot of water sample, typically 40 mL, is transferred into a 60 mL Teflon vial (for high MMHg concentration samples, small sample size should be used, but bring the final volume to a known volume with DDW). Add 0.2 mL of the 20% KCl/0.2 % L-Cysteine solution and 0.5 mL of 9 M H_2SO_4. Start the distillation immediately after addition of reagents at a nitrogen flow rate of approximately 73 $mL{\cdot}min^{-1}$ and at a heating block temperature of 145° C. The distillate is collected in a 60 mL Teflon vial containing 5 mL of 0.05% $NH_2OH{\cdot}HCl$ in DDW, which is cooled in an ice-water bath. The distillation is finished when approximately 85% of distillate is collected after taking 2-3 hours. Bring the final volume of the receiving vial to the 58 mL mark with DDW. Depending on its MMHg concentration, transfer the whole or an aliquot of the distillate into the methylation reaction vessel for analysis as described in section 4. Note: Open the flow of nitrogen up to one hour before beginning the distillation to purge the lines of room air and other possible contaminants.

6.1.2. Solvent extraction

Reagent: 30% KCl (saturated), methylene chloride (large blanks in MMHg determination occasionally result from this solvent. Therefore, different brands and lot numbers should be examined to minimize this contamination.)

Extraction procedure: An extraction procedure described by Bloom (1989) was used. Depending on its concentration, weigh an approximate volume of the sample acidified to a pH of 2-5, typically 50 mL into a 125 mL Teflon bottle. If a smaller sample size is used, bring the final volume to 50 mL with DDW. Add 5 mL of 30% KCl, and swirl the bottle to mix. Add 40 mL of methylene chloride.

Shake the bottle for 1-2 h with a mechanical shaker to reach a distribution equilibrium of MMHg between aqueous and solvent phases, then allow the two phases to separate. Remove the upper phase (aqueous phase) by pipetting. Add about 50 mL of DDW to the methylene chloride, and place the uncapped bottle in a hot water bath at 60° C until all of the CH_2Cl_2 has boiled away. Be aware that the methylene chloride can boil suddenly in bursts, sending water and solvent into nearby bottles. Slowly bringing the bath up to temperature can hinder this effect. Watch the bottles to see if a steady boiling arises; if not, try rearranging the bottles (heat may be unevenly distributed on the bath floor if using an electric skillet). After all visible solvent has evaporated, continue heating for ten minutes. Then purge the water for 2-3 minutes at 250 $mL \cdot min^{-1}$ with Hg free N_2 to remove any residual solvent. The MMHg is transferred to the DDW matrix, which is ready for ethylation as described above. At least 2 reagent blanks and 2 spikes are run each day of extraction/analysis. Usually, 10% of samples are used for spike recovery evaluation. The mean recovery is calculated, which is used to correct all sample results.

6.2. Preparation of biological materials and sediments for MMHg.

6.2.1. Alkaline digestion: Weigh about 0.1 gram of biological material (wet, homogenous) into a 2.5 mL Teflon vial. Add 1.0 mL of 25% KOH methanol solution and cap the vial tightly. Digest the sample in an oven at 65° C for 3-4 hours. Avoid heating overnight, as recoveries drop sharply; recoveries may return to expected levels after sitting for several hours at room temperature. After digestion, bring the final volume to 2.5 mL with methanol prior to analysis. Analyze an appropriate aliquot, depending on the sample's concentration of MMHg and Hg(II). The day of analysis (if different from day of preparation), samples should be shaken thoroughly, heated in the oven at 65° C for 15-20 minutes and aliquots analyzed after samples have cooled and particulate settled. Alternatively, the digestion may be scaled up if larger volumes are required. One gram may be weighed into a 25.6 mL vial, and 10 mL of 25% KOH methanol solution added prior to digestion.

6.2.2. Distillation: Sediment samples should be distilled directly by weighing an appropriate amount, typically 1 gram, into a 25.6 mL Teflon vial and adding 15 mL of DDW. Distill as per the procedure mentioned above (6.1.1). If for biological samples, the MMHg concentration compared to Hg(II) is low, matrix interference on ethylation reaction caused by using large volumes of alkaline digestate will occur. This interference is avoided by distillation (Horvat, Bloom, and Liang, 1993). Distill after alkaline digestion by transferring 0.5-2.0 mL of alkaline digestate into a 25.6 mL vial, adding 15 mL DDW and following section 6.1.1.

7. SAMPLE COLLECTION, STORAGE, AND HANDLING, AQUEOUS, SEDIMENTS, AND BIOLOGICAL MATERIALS.

7.1. Water

7.1.1. Samples should be collected only into rigorously cleaned Teflon bottles. Under no circumstances should ordinary plastic (i.e.; polyethylene, polypropylene, or vinyl) containers be used, as they are very diffusive to gaseous Hg(0) from the air. Ashed or rigorously acid cleaned Borosilicate or quartz glass bottles with Teflon caps may be used as well. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Gill and Fitzgerald, 1985). As an added precaution, clean bottles are filled with high purity 1% HCl solution and capped, dried, and double-bagged in new zip-loc bags in the clean-room, and stored in wooden or plastic boxes until use.

7.1.2. Samples are collected using rigorous, ultra-clean protocols (Gill and Fitzgerald, 1985; and EPA Method 1669 "Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels", April 1995) which are summarized as follows:

a) At least two persons wearing fresh clean-room gloves at all times, are required on a sampling crew.

b) One person ("dirty hands") pulls a bagged bottle from the box, and opens the outer, dirty bag, avoiding touching inside that bag.

c) The other person ("clean hands") reaches in, opens the inner bag, and pulls out the sample bottle.

d) The bottle is opened with a plastic shrouded dedicated wrench, and the acidified water is discarded downstream of the sampling site.

e) The bottle is rinsed once with sample water, and then filled.

f) Preservative (i.e.; 0.8% by volume of high purity HCl) may be added at this time, or within several hours after receipt at the clean laboratory.

g) The cap is replaced with the wrench, and the bottle rebagged in the opposite order from which it was removed.

h) Clean-room gloves are changed between samples and whenever something not known to be clean is touched.

i) Water samples are best obtained by surface grab, using gloved hands, and facing into a flowing body of water (i.e.; looking upstream or of the bow of a moving boat). If samples are to be taken from depth, the only non-contaminating method generally available is pumping. Two methods have been found to work in this regard. The first is to use rigorously acid-cleaned Teflon tubing, and a peristaltic pump with *freshly cleaned*

(heating to 70° C in 5% HCl + CH_3COOH) silicon tubing. Beware that once cleaned, silicon tubing quickly absorbs Hg from the air The other method involves high-volume pumping (i.e.; 50 $L \cdot min^{-1}$) through neoprene hose. If this method is used, it is best to clean the system first by pumping several hundred liters of 5% HCl solution, and then pumping clean water for several hours. This second technique works largely because the rate of flow is so fast that the contamination becomes imperceptibly diluted.

j) DISCRETE SAMPLERS, i.e.; Niskin, GoFlo, and Kemerer BOTTLES, ARE TO BE AVOIDED, AS EVEN UNDER THE BEST OF CONDITIONS THEY ARE OFTEN FOUND TO GROSSLY CONTAMINATE SAMPLES AT THE $ng \cdot L^{-1}$ LEVEL.

7.1.3. Samples may be preserved by adding 8 $mL \cdot L^{-1}$ of concentrated HCl (if only total methylmercury is to be analyzed), or frozen if labile and methylmercury are to be analyzed. Samples may also be sent back to the laboratory unpreserved if they are 1) collected in Teflon bottles, 2) filled to the top with no head space, and 3) sent at 1° C by overnight mail. The samples should be preserved and analyzed soon after arrival at the laboratory (within 24 hours). FREEZING IS NOT AN ACCEPTABLE TECHNIQUE FOR TOTAL INORGANIC Hg, AS UPON THAWING, MUCH Hg(II) IS CONVERTED TO VOLATILE Hg^0.

7.1.4. All handling of the samples in the lab is to occur by clean-room gloved personnel in a class-100 clean room station with mercury removal filters, after rinsing the outside of the bottles in low Hg water, and drying in the clean air hood.

7.2. Solids

7.2.1. Samples should be collected only into rigorously cleaned Teflon containers or glass containers with Teflon lined lids. Under no circumstances should polyethylene, polypropylene, or vinyl containers be used.

7.2.2. Samples are to be frozen at <-10°C (standard freezer on coldest setting) until use. A holding time of 1 year at <-10°C is recommended.

7.2.3. All dissection, homogenization, and other handling of the samples is to occur by clean-room gloved personnel in a class-100 clean room station with mercury removal filters.

8. QUALITY CONTROL

8.1. All quality control data should be maintained and available for easy reference or inspection.

8.2. Calibration data must be composed of a minimum of 2 calibration (or bubbler) blanks and 3 standards (preferably four of each). Such a calibration should be run when stock standards have been remade, conditions have changed, or initial calibration checks defined in section 8.4 do not yield acceptable recoveries.

8.3. Samples containing high analyte concentrations may be run either following dilution, or on a separate run at lower instrumental sensitivity provided the instrument is calibrated at this sensitivity. All peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed in the calibration curve and above the lowest standard if possible.

8.4. Calibration checks must be analyzed after instrument calibration (or at the beginning of analysis), after every ten samples and at the end of the analytical batch. Calibration checks shall consist of a mid-level standard and a bubbler (calibration check) blank. Additionally, an initial calibration check obtained from a source independent from that used to obtain the calibration standard must be analyzed after instrument calibration (or the beginning of analysis). The calibration check standard and independent calibration check standard must be within 20% of the calibration and the calibration check blank must contain no more than 4.0 pg MMHg.

8.5. Method detection limits for each preparation method and/or matrix are determined by 40 CFR 136, Appendix B using a minimum of seven replicate analyses of an appropriately prepared matrix.

8.6. A minimum of 2 method blanks per batch of 20 samples must be run. Method blank results are entered into a quality control chart and trends are monitored. An alternative method detection limit may be obtained using the standard deviation estimated from at least 7 sets of method blanks. Method blanks should consist of all reagents used for a sample and should be carried through the entire method as a sample. To estimate the standard deviation from multiple sets of duplicate method blanks, the following formula is used:

$$\text{Estimated Standard Deviation} = \sqrt{[\sum(d \cdot d)] / 2m}$$

where d is the difference between within batch determinations of the method blanks and m is the number of duplicate blank determinations.

8.7. Method duplicate analysis should be performed once every 10 samples or once per batch, whichever is greater. Duplicate samples are defined as a homogeneous sample that is split into two aliquots, and then each aliquot is carried through the entire preparation and analytical procedure. The criterion for duplicate sample precision is determined by control charts. If control charts are not available then the duplicate sample

results must have a relative percent difference of 35% or less for water and 35% or less for solids for the analysis to be considered valid. Precision results not meeting these criteria shall be reprepared and reanalyzed or qualified at the discretion of the lab director.

8.8. NRC or NBS certified reference materials for mercury in tissues and sediments should be analyzed at a frequency of once per 10 samples or once per batch, whichever is greater. Criteria for CRM recoveries are determined by control charts. If control charts are not available then CRM results should be within 35% of the certified value for the analysis to be considered valid. CRM accuracy results not meeting this criterion shall be reprepared and reanalyzed or qualified at the discretion of the lab director.

8.9. Matrix spike analysis should be performed once every 10 samples or once per batch, whichever is greater. A matrix spike sample is defined as an aliquot of homogenized sample that has a known amount of analyte added to it. The matrix spike sample is then processed through the entire preparation and analytical procedure. Bias is then determined by calculating the percent recovery of the known amount.

Percent recovery = 100 * (spiked sample result (conc.) - sample result (conc.)) / (amount spiked)

The criterion for spike recovery is determined by control charts. If control charts are not available. then the spike recovery must be within the range 65-135%. Matrix spike duplicate samples may be analyzed at the request of the client. The criterion for spike duplicate sample precision is determined by control charts. If control charts are not available then the spike duplicate sample results must have a relative percent difference of 35% or less for water and 35% or less for solids for the analysis to be considered valid. Precision and accuracy results not meeting these criteria shall be reprepared and reanalyzed or qualified at the discretion of the lab director.

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MMHg Analysis Sheet

☐MMHg ☐Other:_____ Batch:_____ Matrix:_____

Analyst:_____ Calibration Blank $\bar{X}$:_____ Blank Corr. Calib. Coef. $\bar{X}$:_____
Date:_____ Method Blank $\bar{X}$:_____ Pretrap:_____ RSD:_____
Instrument ID # _____ Standards 1 ng/mL:_____ Buffer:_____ N=:_____
QA: Full☐ Standard☐ 0.1 ng/mL:_____ $NaBEt_4$_____ r:_____

Run	Trap	Sample ID	Sample vol/wt.	Dilution Volume	Analyzed volume	Raw PA	pg	Result

Calculation Equation:_____
Comments:_____

Independent Source Std.:_____ Method SRM:_____

MMHg Analysis Sheet

Batch:_____ Analyst:_____ Date:_____

Run	Trap	Sample ID	Sample vol/wt.	Dilution Volume	Analyzed volume	Raw PA	pg	Result

METHYLMERCURY EXAMPLE ANALYTICAL RUN SEQUENCE
(minimum frequency requirements)

RUN	Analyze	Description	Requirements
01	Calibration Blank (CB)		≤4.0 pg
02	Calibration Blank (CB)		≤4.0 pg
03	Calibration Blank (CB)		≤4.0 pg
04	10 pg std.	Calibration	Correlation
05	50 pg std.	Curve*	Coefficient (r)
06	100 pg std.	"	>0.995
07	250 pg std.	"	RSD≤15%
08	1000 pg std.*	"	
09	mid-level calibration check	Independent Source	80 – 120% recovery
10	mid-level calibration verification (ICV)	Standard Source	80 – 120% recovery
11	Initial Calibration Blank Check (ICB)		≤4.0 pg
12	Method Blank 1 (MB-1)	Method Blank	Calib blank corr. conc. ≤MDL
13	Method Blank 2 (MB-2)	Method Blank	Calib blank corr. conc. ≤MDL
14	CRM-1	Reference Material	Refer to current CQAP
15	CRM-2	Reference Material	for accuracy control limits
16	Sample 01	Native Sample	
17	Sample 01MD	Matrix Duplicate	RPD ≤ 35% for water and solid
18	Sample 02	Native Sample	
19	Sample 02MS	Matrix Spike**	Refer to current CQAP for accuracy control limits
20	Sample 03		
21	Sample 04		
22	mid-level calibration verification (CCV)	Standard Source	80 – 120% recovery
23	Blank Check (CCB)		≤4.0 pg
24	Sample 05		
25	Sample 06		
26	Sample 07		
27	Sample 08		
28	Sample 09		
29	Sample 10		
30	Sample 11	Native Sample	
31	Sample 11MD	Method Duplicate	RPD ≤ 35% for water and solid
32	Sample 12	Native Sample	
33	Sample 12MS	Matrix Spike	Refer to current CQAP for accuracy control limits
34	CCV	Standard Source	80 – 120% recovery
35	CCB		≤4.0 pg
36	Sample 13		
37	Sample 14		
38	Sample 15		
39	Sample 16		
40	Sample 17		
41	CCV	Final Calib. Check – Standard Source	80 – 120% recovery
42	CCB		≤4.0 pg

* Calibration Curve may be adjusted depending on expected range of samples (i.e. seds and biota 10pg-5000pg)

** Clients may request MS and/or MSD (Matrix Spike Duplicate), in which case lab personnel will be notified.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

STANDARD OPERATING PROCEDURE (M007b)
EPA METHOD 200.7
TRACE ELEMENT ANALYSIS USING ICP

Applicable matrix or matrices: Aqueous Samples
Standard Compound List and Reporting Limits: Refer to Table 1 and Table 2

Approvals and Signatures

QA Director: _____ **Date:** 12/27/01

Laboratory Director: _____ **Date:** 12·27·01

Department Manager: _____ **Date:** 12/27/01

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1.0 SCOPE AND APPLICATION

1.1 This SOP enumerates the steps and conditions involved in operation of the Thermo Jarrell Ash ICAP 61E and the analytical protocol. Samples are analyzed after the appropriate digestion procedure is performed according to those Standard Operating Procedures.

1.2 This Method is applicable to Drinking Water, Surface Water, Domestic and Industrial Wastewater. This method may be used for compliance with the Safe Drinking Water Act and the Clean Water Act. Note that it may not always be possible to meet the State Drinking Water Required Detection Limits for Reporting (DLR) for some of the elements listed below. Samples for drinking water analysis should not be diluted or it may be necessary to utilize Method 200.8. The elements for which this analytical protocol was developed and approved for drinking water and wastewater are the following:

Table 1: Elements

Aluminum	Arsenic	Barium	Antimony (Wastewater only)
Beryllium	Cadmium	Calcium	Boron* (Wastewater only)
Chromium	Copper	Iron	Cobalt (Wastewater only)
Magnesium	Manganese	Nickel	Lead (Wastewater only)
Potassium	Silver	Silicon (as SiO_2)	Molybdenum (Wastewater only)
Sodium	Zinc		Selenium (Wastewater only)
Thallium (Wastewater only)	Tin* (Wastewater only)	Titanium* (Wastewater only)	Vanadium (Wastewater only)

*Elements added to method.

The wavelengths and Reporting Limits are indicated in Table 2.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

Note: The quality control limits specified in this Standard Operating Procedure are applicable to all analyses which specify this method and are not governed by a project or program specific QAPP. In cases where a separate QAPP is provided, the QAPP will supersede the limits specified herein.

2.0 SUMMARY OF METHOD

2.1 An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multielemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line mission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis.

3.0 DEFINITIONS

3.1 **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument (Sect.7.8.1).

3.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration (Sect. 7.10).

3.3 **Field Reagent Blank (FRB)** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment (Sect 8.5).

3.4 **Instrument Detection Limit (IDL)** - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

3.5 **Instrument Performance Check (IPC) Solution** - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Sects. 7.11 & 9.3.4).

3.6 **Internal Standard** - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.7 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements (Sects. 7.8.3 & 9.3.2).

3.8 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations (Sect. 9.4.2).

3.9 **Laboratory Reagent Blank (LRB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Sects. 7.8.2 & 9.3.1).

3.10 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear (Sect. 9.2.2).

3.11 **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Sect. 9.2.4 and Table 1).

3.12 **Plasma Solution** - A solution that is used to determine the optimum height above the work coil for viewing the plasma (Sect. 7.16).

3.13 **Quality Control Sample (QCS)** - A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance (Sect. 9.2.3).

3.14 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

3.15 **Spectral Interference Check (ICS) Solution** - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria (Sects. 7.13, 7.14 & 9.3.5).

3.16 **Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source (Sect. 7.9).

3.17 **Total Recoverable Analyte** - The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of < 1 NTU (Sect. 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sects. 11.2 & 11.3).

3.18 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

4.1 Spectral Interferences

4.1.1 Overlap of a spectral line from another element. Spectral overlap is compensated for by correcting the raw data after monitoring and measuring the interfering element via the application of Inter Element Correction factors (IECs).

4.1.2 Unresolved overlap of molecular band spectra. Unresolved overlap requires selection of an alternate wavelength.

4.1.3 Background contribution from continuous or recombination phenomena. Background contribution and stray light can usually be compensated for by background correction adjacent to the analyte line.

4.1.4 Stray light from the emission of a high-concentration of elements.

4.2 Physical Interferences

4.2.1 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high levels of dissolved solids or high acid concentrations. Diluting the samples can reduce physical interferences and the effects minimized by adding an internal standard such as Yttrium or Scandium to all standards and samples.

4.3 Serial Dilution: If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limits after dilution), the serial dilution (a four to five-fold dilution) should agree within 10% of the original determination. If the dilution analysis is greater than 10%, chemical or physical interferences are suspected.

4.4 Post Digestion Spike Addition: (performed as per Client request) The recovery of spike addition added at the minimum level of 10x the instrumental detection limit should be recovered within 75-125 % or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of standard addition analysis can compensate for this effect.

4.5 Comparison with alternate method of analysis: When investigating a new matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methods.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

5.0 SAFETY

5.1 During the execution of the procedures outlined in this SOP, potentially hazardous compounds may be encountered. Preparation personnel should observe all appropriate safety rules as outlined in the Chemical Hygiene Plan.

5.2 Samples handled under this SOP may originate from unknown sites, which could contain a variety of hazardous materials. Appropriate safety rules as outlined in the Chemical Hygiene Plan should be observed while handling samples of unknown content and/or origin.

6.0 EQUIPMENT AND SUPPLIES

6.1 Thermo Jarrell Ash Inductively Coupled Argon Plasma Spectrometer (TJA ICAP-61E).

6.2 PC Computer running ThermoSpec software, with printer.

6.3 Autosampler.

6.4 Pump Tubing. There are two different diameters of pump tubing. The larger one (red/red) is used for the line from the rinse container to the auto-sampler rinse station. The smaller one (orange/orange) is used between the Teflon tubing from the sipper and the Teflon tubing leading to the nebulizer.

6.5 Test Tubes. The size used for the ICP is 17 X 100 mm. Be sure to use plastic (any pre-cleaned or sterile plastic test tube is OK).

6.6 Filter Paper. Whatman 40 or finer pore size. All samples must be free of particulates before analysis. Filter at bench-top when necessary.

6.7 In-line argon filter. This filter is essential to keep dust particles in the argon line from plugging the nebulizer. While they only need to be replaced on a semi-annual basis, extra stock should be maintained.

6.8 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

6.9 A temperature adjustable hot plate capable of maintaining a temperature of 95-C.

6.10 (optional) A temperature adjustable block digester capable of maintaining a temperature of 95-C and equipped with 250-mL constricted digestion tubes.

6.11 (optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.12 A gravity convection drying oven with thermostatic control capable of maintaining 180-C + 5-C.

6.13 (optional) An air displacement pipetter capable of delivering volumes ranging from 0.1 to 2500 µL with an assortment of high quality disposable pipette tips.

6.14 Mortar and pestle, ceramic or nonmetallic material.

6.15 Polypropylene sieve, S-mesh (4 mm opening).

6.16 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 h or more in 20% (v/v) nitric acid or a mixture of HNO3 and HCl (1+2+9), rinsing with reagent water and storing 2,3 Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.16.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).
6.16.2 Assorted calibrated pipettes.
6.16.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250-mL with 50-mm watch glasses.
6.16.4 Griffin beakers, 250-mL with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.
6.16.5 (optional) PTFE and/or quartz Griffin beakers, 250-mL with PTFE covers.
6.16.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.
6.16.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-mL to 1-L capacities.
6.16.8 One-piece stem FEP wash bottle with screw closure, 125-mL capacity.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.
7.2.1 Hydrochloric acid (1+1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.
7.2.2 Hydrochloric acid (1+4) - Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.
7.2.3 Hydrochloric acid (1+20) - Add 10 mL concentrated HCl to 200 L reagent water.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

7.3 Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

7.3.1 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.3.2 Nitric acid (1+2) - Add 100 mL concentrated HNO_3 to 200 mL reagent water.

7.3.3 Nitric acid (1+5) - Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.4 Nitric acid (1+9) -Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.4 **Reagent water** – Use the 18 megohm deionized water supply. The conductivity of the water must be monitored daily and recorded in a conductivity logbook. Reagent water shall have a conductivity of less than 1.0 µS/cm. If the conductivity limits are exceeded, replace the resin beds in the Nanopure DI unit.

7.5 Ammonium hydroxide, concentrated (sp. gr. 0.902).

7.6 Tartaric acid, ACS reagent grade.

7.7 Hydrogen peroxide, 50%, stabilized certified reagent grade.

7.8 Blanks - Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure, the laboratory fortified blank is used to assess routine laboratory performance and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.8.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to 2% with HNO_3 The calibration blank should be stored in a FEP bottle.

7.8.2 The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in the processing of the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.8.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to a suitable concentration using the following recommended criteria: Ag <= 0.1 mg/L, >= K 5.0 mg/L and all other analytes 0.2 mg/L or a concentration approximately 100 times their respective MDL, whichever is greater. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.8.4 The rinse blank is prepared by acidifying reagent water to 5% with HNO_3. There should be a large container of ICP rinse under the instrument, and a plastic bottle of this blank solution is used for digestate dilution.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

7.9 Stock Calibration Standards

7.9.1 Stock standards are purchased commercially through Solutions Plus, CPI, and Ultra Scientific.

7.9.2 **QC-7 and QC-19 multi-element stock calibration standards are used which contain the majority of the standards routinely analyzed.**

7.9.3 **Single element stock solutions are used for Al, Ca, Fe, Mg, Na, K, Si (reported as SiO2), Sr, and Sn. (A single element standard of silicon is used to supplement the low concentration present in the QC-7 multi-element solution.)**

7.10 Calibration Standards

7.10.1 Single Point Calibration Standards.

7.10.1.1 Three calibration standards are used, S6, S3 and S0. S6 contains Al, Ca, Fe, Mg, Na, and K at 100,000 µg/L.
S3 contains all other elements in Table 1 at a concentration of 2,000 µg/L. S0 is laboratory reagent water.

7.10.2 Multiple Point Calibration Standards

7.10.2.1 Seven calibration standards are used, S6, S5, S4, S3, S2, S1 and S0. S6, S5, S4 contain Al, Ca, Fe, Mg, Na, and K at 100,000 µg/L, 50,000 µg/L, and 25,000 µg/L respectively. S3, S2, and S1 contain all other elements in Table 1 at concentrations of 2,000 µg/L, 1,000 µg/L, and 500 µg/L, respectively. S0 is laboratory reagent water.

7.11 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Silver must be limited to < 0.5 mg/L; while potassium and phosphorus because of higher MDLs and silica because of potential contamination should be at concentrations of 10 mg/L. For other analytes a concentration of 2 mg/L is recommended. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.12 ICV/CCV Calibration Check Solution. This solution contains every metal at the midrange point of the calibration and is a second source custom multi-element standard. The concentrations are indicated in Table 4.

7.13 Interference Check Solutions. These solutions, are Inter-element Correction Samples A and AB (ICSA and ICSAB). The ICSA solution contains interfering elements at various concentrations as indicated in Table 4. ICSAB contains both interfering elements and all other elements at concentration indicated in Table 4. The run order of these two samples is always ICSA then ICSAB.

7.14 Contract Reporting Detection Limit (CRDL) Standard. A multi-element check standard prepared at various concentrations equal to the Reporting Limit (RL) as indicated in Table 4.

7.15 Plasma Solution - The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Sect. 10.2). The solution is prepared by adding a 5-mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) nitric acid and 20 mL (1+1) hydrochloric acid and diluting to 500 mL with reagent water. Store in a FEP bottle.

Note – Each new lot of acid or solvent must be checked for contamination by using a method blank. These blanks must pass below the reporting limit for each new lot. If a new lot is found to be contaminated it shall not be used. It is recommended that the vendor set aside a number of bottles of the same lot to minimize the number of blanks analyzed.

8.0 SAMPLE COLLECTION, PRESERVATION. AND STORAGE

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45-um pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus is recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) nitric acid immediately following filtration to pH < 2.

8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1:1) nitric acid to pH < 2 (normally, 3 mL of (1:1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory.

Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2. See Section 8.1.

NOTE: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

8.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 QUALITY CONTROL REQUIREMENTS

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

9.2 Initial Demonstration of Performance (mandatory).

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

9.2.2 Linear dynamic range (LDR) - The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing succeedingly higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs should be verified annually or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.3 Quality control sample (QCS) - When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Sect.7.12). To verify the calibration standards the determined mean concentrations from 3 analyses of the QCS must be within +/- 5% of the stated values. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL) - MDLs must be established for all wavelengths utilized, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.15 To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. If the relative standard deviation (RSD) from the analyses of the seven aliquots is < 10%, the concentration used to determine the analyte MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Sect. 9.4.2) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Sect.1.2). MDLs should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 **Laboratory Reagent Blank (LRB)** - For each analytical batch of no more than 20 samples processed, a LRB (method blank) must be carried throughout the entire sample-preparation and analytical process. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute 10% or more of the analyte level determined for a sample or is above the RL (Reporting Limit) whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

9.3.2 **Laboratory Fortified Blank (LFB)** - must be processed with each analytical batch of no more than 20 samples. An LFB is a blank spiked at approximately ten times the method detection limit and brought through the whole preparation and analytical process. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 Use LFB analyses data to assess laboratory performance against the required control limits of 85-115% (Sect.9.3.2). When sufficient internal performance data become available (usually a minimum of twenty to thirty analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent twenty to thirty data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance - For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, run the calibration blank and ICV/CCV before and after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The analysis of all analytes within the standard solutions must be within 10% of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. (The instrument responses from the calibration check may be used for recalibration purposes, however, it must be verified before continuing sample analysis.) If the continuing calibration check is not confirmed within 10%, the previous 10 samples must be reanalyzed after recalibration. If the sample matrix is responsible for the calibration drift, it is recommended that the previous 10 samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Sect 9.4.2) is required.

9.4.2 **Laboratory Fortified Sample Matrix (LFM)** - Add a known amount of each analyte to a minimum of 5% (in the case of drinking waters, 10%) of the routine samples. Spiked samples should be included whenever a new sample matrix is being analyzed. If there is insufficient sample for a LFM duplicate, then a LFB duplicate may be substituted. In each case the LFM and LFMD aliquots must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Sect. 9.3.2). For solid samples, however, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L x 0.1L/0.00 0lkg = 100, Sect. 12.1). Over time, samples from all routine sample sources should be fortified.

NOTE: The concentration of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at the same concentration used for the LFB may prove to be of little use in assessing data quality for these analytes. For these analytes sample dilution and reanalysis is recommended. Also, if specified by the data user, laboratory or program, samples can be fortified at higher concentrations, but even major constituents should be limited to < 25 mg/L so as not to alter the sample matrix and affect the analysis.

9.4.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70-130% or a 3 sigma recovery range calculated from regression equations. Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. Percent recovery should be calculated in units appropriate to the matrix.

Accuracy (Percent Recovery)

$$\%Rec = \frac{\text{(Concentration of LFM} - \text{Concentration of Sample)}}{\text{Spike Concentration Added}} \times 100$$

Precision (Relative Percent Difference)

$$RPD = \frac{\text{(Concentration of LFM} - \text{Concentration of LFMD)}}{\text{(Concentration of LFM} + \text{Concentration of LFMD)} / 2} \times 100$$

9.4.4 If the recovery of any analyte falls outside the designated recovery range, and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or an uncorrected matrix effects.

9.4 A sample duplicate should also be performed with each analytical batch of no more than 20 samples. A sample duplicate is a sample brought through the whole sample preparation and analytical process.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

10.0 CALIBRATION AND STANDARDIZATION

10.1 Operating Conditions:

10.1.1 Before igniting the plasma, check the following:

10.1.1.1 The vacuum gauge should read 15 ATM or less.

10.1.1.2 The two red lights (SB and FAT) at the left in the Controller Panel should be ON.

10.1.1.3 The autosampler rinse station and nebulizer waste carboys must have sufficient head space.

10.1.1.4 Visually inspect the torch.

10.1.2 Instructions for cold start up of the instrument/software system are as follows: (These steps must be followed after a power failure, a full power shutdown, or whenever the ICP computer has been used to attach to the lab network in any way. Any other glitch in the plasma control software also indicates a need for this reset.):

10.1.2.1 Turn off the computer. Be sure it is in TJA and not NET mode. If in doubt, type GOTJA and hit enter before turning off the computer. You will get a prompt to reboot. The monitor and printer can remain on. Be sure to form-feed the printer if it is not at a page break.

10.1.2.2 Turn off the autosampler. Wait 10 seconds, then turn it on again. The sipper should be in the rinse position.

10.1.2.3 On the back of the instrument, press the red reset button. On the front of the instrument, press the black reset button just above the mercury venire. Press these buttons twice each, going back to front each time. Wait 3-5 seconds before pressing each button during this sequence. There should be a noticeable click from the torch box area every time the front reset button is pushed.

10.1.2.4 Turn the computer back on. It should ask for date, time, and then automatically start ThermoSpec.

10.2 Run Setup for the ICP:

10.2.1 Connect the autosampler pump tubing for samples and rinse station. Be sure the extra bridge on the orange/orange tubing is between the pump and the nebulizer.

10.2.2 Make sure 5% HNO_3 rinse solution reservoir has sufficient volume for the analysis.

10.2.3 Using the arrow keys, go to the Setup module and select the Plasma Control Panel. Alternatively, press U (set Up), then P (Plasma control panel).

10.2.4 Press **F1 <STARTUP>** and **F9 <CONTINUE>**. There will be a 90-second purging time, after which the plasma will automatically ignite. A blue message will appear on the screen asking if you wish to continue. Press **<ENTER>** to continue, then press **F2 <LEVELS>**. Change the pump rate to 100 and press **<ENTER>**. This will start the pump. Change PSI to 30, Auxilary Gas to medium, and press **<ENTER>**. When the nebulizer pressure has been changed successfully (you may have to do it twice), press **F9 <DONE/KEEP>** and then **<ESC>**. This will take you back to the main menu.

10.2.5 Go to Development and select Methods. Type in **20076010** for the multi-point method used for all metals analyses, then press **<ENTER>**. Press **F3 <METHOD INFO>** and change the Analysis Data File and Autosampler Table names. This name will reflect the date and run of the day: for instance, **W121299** is the first run of the day on December 12, 1999. Press **F9 <DONE/KEEP>** twice and you will be back to the main menu.

10.2.6 Create the Autosampler Table by either copying an existing table and removing the unknown samples or create a new table from). Table 5 contains a typical autosampler table.

10.2.6.1 To copy an existing table, go to IMS menu and select Filer. Select **5 <Autosampler Tables>**. Select previous Autosampler Table by number and then press **F8 <COPY>**. Name Autosampler Table current date and then press **<ENTER> <ENTER>**. Press **<ESC>, <ESC>** to exit Filer.

10.2.6.2 Go to Operation and select Autosampler Setup. Enter the Autosampler Table name and **<ENTER>**. Press **F1 <Edit Set>** and then **F1 <EdSamples>**. Delete all the samples below the ICB by using the down arrow to go to the first sample to delete and then press **F2 <Delete>**. Press **F1 <InsSamples>** enough times for the samples to be analyzed. For each Sample enter the sample ID as it appears on the bench worksheet. If a sample is diluted, the dilution factor is entered after the sample ID. Do not enter the dilution factor anywhere else in the autosampler table because ELM and Autoposting will not work correctly.

NOTE: It may be difficult to achieve the State Required Detection Limits for Reporting (DLR) for some compounds if samples are diluted. Care should be given to not dilute samples unnecessarily when samples are being analyzed for compliance with the Safe Drinking Water Act.

10.2.7 Alternatively to copying an existing autosampler table and modifying it, you can create a brand new autosampler table. Go to the Operation menu and select Autosampler Setup. Enter the new autosampler table name and <ENTER>. Press F3 <ADDSET>. Enter the Method Name, Default Operator I.D., a 90 second rinse time, and the number of unknowns (from your ICP worksheet). Arrow down to *"Default Sample Name"* and press the space bar to delete the words *"Sample-1"*. Arrow over to *Auto-increment* and press the space bar to change *Yes* to *No*. Now press F1 <EDSAMPLES>. Press F5 to insert your standards at the beginning of the table. For each Sample enter the sample ID as it appears on the bench worksheet. If a sample is diluted, the dilution factor is entered after the sample ID.

10.2.8 After all samples are entered, add the QC samples and appropriate check tables. Add CCV, CCB, ICSA and ICSAB according to Quality Control Rules (see section 11). Add check tables by arrowing over to the column filled with the words FromMtd. Overwrite this entry for the QC samples using the following rules: ICV, ICB, CRDL, ICSA, ICSAB, CCV, CCB, BLK1, BS1 all have check tables that can be used. The names of the tables to use are in table 4. After assigning the appropriate check tables, save the autosampler table by pressing **F9 <DONEKEEP>** twice. Press **<F2>** to print the Autosampler Table. Press **F9 <DONEKEEP>** once more to return to the main menu.

10.3 Analysis Set UP Using the ICP:

10.3.1 Go to Operation and select Analysis. Accept the **20076010** method if it pops up, and type **20076010** if it doesn't. Press **<ENTER>**.

10.3.2 Press F5 **<Profile>** and the Profile screen will appear. Open the door of the optical path and open the mercury lamp window (leave the door open while running the profile...this will remind you to turn OFF the mercury lamp when profiling is complete. Leaving the mercury window open may introduce strong spectral interferences due to the high intensity of the beam). Press **F3 <Automatic>**, then **F1 <Run>** to profile. . The profile should be between -1 and 1. If the value is too negative (-1.20), adjust the venire UP. If the value is too high adjust the venire DOWN.

If an adjustment has been made, press **<ESC> <ENTER> <F3> <F1>** to do another profile. When the profile is acceptable, press **F9 <Done>** and close the mercury lamp window.

10.3.3 Using the printout of the Autosampler Table, fill the autosampler rack during and after the profile. Fill the calibration standards first and then the digested samples. If the profile is done by now, go ahead and start the run before pouring out the actual samples.

10.3.3 Press **F9 <AUTOSAMPLER>**. The cursor will be flashing at the autosampler table name. Press **<ENTER>**. If the instrument is to be run in shutdown mode, press **F7 <TermAction>** to toggle the Terminating Action to Shutdown. Do one last scan of the instrument. Confirm that the pump is drawing smoothly, that there is a good "cloud" in the spray chamber and that the plasma is steady. Verify that the waste containers are sufficiently empty and that the rinse container is sufficiently full. If everything is OK, press **F1 <RUN>** to run the ICP. Try to make sure the fanfold paper is stacking correctly before leaving the instrument to run alone. (Minimum warm up time of 40 minutes.)

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (>/- 20 mL) of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis (Sect. 11.4). Allowance for sample dilution should be made in the calculations. (If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects.

NOTE: If a precipitate is formed during acidification transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 thru 11.2.7 prior to analysis.

11.2 Aqueous Sample Preparation - Total Recoverable Analytes

11.2.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 11.1.1 while making allowance for sample dilution in the data calculation. For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis follow the procedure given in Sections 11 .2.2 through 11. 2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples (other than drinking water with < 1 NTU turbidity),transfer a 100-mL (+/-1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker (When necessary, smaller sample aliquot volumes may be used.)

NOTE: If the sample contains undissolved solids > 1%, a well mixed, acid preserved aliquot containing no more than 1g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11 .3.3 thru 11.3.6.

11.2.3 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85-C. (See the following note.) The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

NOTE: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85-C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95-C.)

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85-C. DO NOT BOIL. This step takes about 2 h for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

11.2.5 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H20 azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-mL volumetric flask, make to volume with reagent water, stopper and mix.

11.2.7 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3 Solid Sample Preparation - Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (> 20g) to tared weighing dish, weigh the sample and record 200.7-31 the wet weight (WW). (For samples with < 35% moisture a 20 g portion is sufficient. For samples with moisture > 35% a larger weight at 60-C and record the dry weight (DW) for calculation of percent solids. (The sample is dried at 60-C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 +/- 0.01 g aliquot (W) of the sample and transfer to a 250-mL Phillips beaker for acid extraction.

11.3.3 To the beaker add 4 mL of (1+1) HNO3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95-C. (See following note.)

NOTE: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85-C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95-C.) Also, a block digester capable of maintaining a temperature of 95-C and equipped with 250-mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 min. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl-H2O azeotrope. Some solution evaporation will occur (3 to 4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100-mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample extract is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.4 Sample Analysis

11.4.1 Prior to daily calibration of the instrument inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

11.4.2 Configure the instrument system to the selected power and operating conditions as determined in Section 10.0.

11.4.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

11.4.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Sect. 7.10) and the calibration blank (Sect. 7.8.1). A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 30 sec after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Sect.7.8.4) for a minimum of 60 seconds between each standard. The calibration line should consist of a minimum of a calibration blank and a high standard. Replicates of the blank and highest standard provide an optimal distribution of calibration standards to minimize the confidence band for a straight-line calibration in a response region with uniform variance.

11.4.5 After completion of the initial requirements of this method, samples should be analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions, LFBs, LFMs, and check solutions.

11.4.6 During the analysis of samples, the laboratory must comply with the required quality control described in Section 9.0. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.7 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and reanalyzed. Also, for the interelement spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, sample dilution with acidified reagent water and reanalysis is required. In these circumstances analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended.

11.4.8 Report data as directed in Section 12.

12.0 CALCULATIONS

12.1 Calculations are performed automatically by the Thermospec Software. Check tables can be created for all of the Quality Control Samples that will flag the data if the data exceeds limits.

13.0 METHOD PERFORMANCE

13.1 Method Detection Limit Studies are performed for this method on each instrument on an annual basis.

14.0 POLLUTION PREVENTION

14.1 All wastes from this procedure shall be disposed following the recommendations of the chemical hygiene plan.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

15.1 Following calibration, a calibration check is performed by reanalyzing the highest calibration standard. The % recovery must be between 94.6 and 105.5%. In the event that this criteria is not met, correct the cause for failure and recalibrate the instrument. Causes of error can include contaminated standards, standards out of order, and/or contaminated blank.

15.2 Following calibration, a linear range check solution is analyzed. The % recovery must be between 94.6 and 105.5%. In the event that this criteria is not met, the linear range for the run is set to the highest standard that meet the 94.6 and 105.5% recovery (generally this is the calibration check from 11.1 above). Causes of error can include contaminated standards, standards out of order, and/or contaminated blank.

15.3 Following calibration, a Contract Reporting Detection Limit (CRDL) Standard is analyzed. This multi-element check standard is prepared at a concentration equal to the Reporting Limit (RL). The recoveries must be between 50.5% and 150.4% of the expected values indicated in Table 3. In the event this criteria is not met, correct the cause for failure and recalibrate the instrument. Causes of error can include contaminated standards, standards out of order, and/or contaminated blank. An ICV/CCV are run at the beginning of the run, following every 10 samples, and the very end of the analytical run. The experimental result must be between 89.5 and 110.5% of the expected value in Table 3. If the result is outside the limits, all data for that element since the last valid ICV/CCV must be rerun after recalibration. Possible causes of failed ICV/CCVs are as follows: clogged lines, crimped tubing, insufficient warm-up time, high salts present in the sample matrices or contamination.

15.4 An ICB/CCB is run after the ICV/CCV at the beginning of the run, following every 10 samples, and the very end of the analytical run. The ICB/CCB is analyzed to assure that there is no carryover or system contamination. The CCB must not exceed +/- the RL. If the CCB does not meet the criteria, take appropriate corrective action and reanalyze associated samples.

15.5 The ICSA and ICSAB are run at the beginning and end of each run. The result for the ICSA must be between 79.5 to 120.5% for all interfering elements and +/- RL for non-analytes. The results for the ICSAB for the non-interfering elements must have a recovery of 79.5% to 120.5%. Probable causes for QC failure are discussed in section 11.4.

15.6 A Method Blank is prepared with every sample batch of twenty samples or less. If the Method Blank is above the DL, appropriate corrective action must be taken.

15.7 A Blank Spike (also referred to as LFB) is prepared with every sample batch of twenty or less. Acceptance criteria are 80-120% of the theoretical value.

15.8 A Laboratory Fortified Sample Matrix (LFM) and a LFM Duplicate are prepared and analyzed for every sample batch of twenty or less. Recoveries generally should be between 75-125%. The relative percent difference between replicate LFM/LFMD should be less than 20%. If the quality control data exceeds these ranges, corrective action must be taken.

15.9 All of these QC samples may be checked automatically by the ICP computer. The "H" or "L" flag is for ICV, CCV, ICB, CCB, BLK1, BS1, ICSA, and ICSAB at levels higher or lower than preset windows. Unless a flag appears on these samples, the data can safely be considered in control.

15.10 Unknown samples may be checked automatically by the ICP computer using a table that checks from –RL to daily Linear Range (61ETAB). "H" or "L" flags will appear on the data for levels higher or lower than preset windows. Unless a flag appears on these samples, the data can safely be considered in control.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

16.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1 Follow the corrective actions outlined in the following table.

Table 2 - Quality Control and Corrective Action

Quality Control Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit (MDL) Study	Annually.	Minimum of 7 replicates. Spike level must be at a concentration between the calculated MDL and 10 x MDL.	Reprepare study at adjusted spiking levels for MDLs falling outside of acceptable range.
Initial Demonstration of Proficiency	Prior to use of method for client samples.	Four replicates of a spiked sample must be prepared and/or analyzed by the chemist. The mean concentration of all compounds must fall within 30% of the expected value. Method-specific. Coefficient of variation for the four replicates must be less than 20%.	Investigate failure. Verify solution integrity and instrument performance. Reprepare and reanalyze.
Ongoing Demonstration of Proficiency	Annually.	Single- or double-blind PE sample within study acceptance range or acceptable MDL study.	Investigate failure. Verify solution integrity and instrument performance. Reprepare and reanalyze.
Initial Calibration.	Daily.	Single point. If a multipoint calibration is requested the correlation coefficient ≥ 0.995.	Check instrument performance. Verify solution integrity. Recalibrate instrument.
Instrument Performance Check	Daily, following initial calibration.	Reanalyze high standard. All compounds must be within 5% of the expected value.	Check instrument performance. Verify solution integrity. Recalibrate instrument.
Initial Calibration Verification (ICV).	Following instrument performance check.	Secondary source at a concentration other than that used in initial calibration. Must be within +/- 10%.	Check instrument performance and perform necessary maintenance. Verify solution integrity. Recalibrate instrument.
Initial Calibration Blank (ICB)	Following ICV.	Must be less than 3x the standard deviation (s) of the mean blank value.	Repeat analysis two more times and average results. If the average is not within 3X of the background mean, terminate analysis, correct the problem, and recalibrate.
Continuing Calibration Verification (CCV)	Following ICV, after every 10 analyses, and at end of analytical sequence.	Must be within +/- 10%.	Check instrument performance and perform necessary maintenance. Verify solution integrity. Recalibrate instrument and reanalyze all samples from last acceptable CCV.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

Quality Control Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Blank (CCB)	Following each CCV, after every ten analyses, and at the end of the analytical sequence.	Must be less than 3x the standard deviation (s) of the mean blank value.	Repeat analysis two more times and average results. If the average is not within 3X of the background mean, terminate analysis, correct the problem, and recalibrate.
Interference Check Sample (ICS)	Following ICV, but prior to sample analysis, and optionally following the analysis of last sample..	All analytes present must be within 20 % of expected value.	Check instrument performance and perform necessary maintenance. Verify solution integrity. Recalibrate and reanalyze all samples since last acceptable ICS.
Preparation Blank	One per preparation batch.	All analytes must be less than 1/2 reporting limit or MDL, whichever is greater.	If analyte concentration in associated samples exceeds blank value by greater than 10 x, then no further action is necessary. If concentration of analyte is less than reporting limit, no further action is necessary. If concentration of analyte in samples is between reporting limit and 10x the blank value, samples must be reprepared and reanalyzed for that analyte(s).
Laboratory Fortified Blank (LFB)	One per preparation batch.	All spiked elements must be +/- 20% of true value.	Reanalyze once. Verify solution integrity and instrument performance. Reprepare and reanalyze all associated samples for failed analyte(s).
Laboratory Fortified Sample Matrix (LFM)	One per 20 field samples of a similar matrix.	All spiked elements must be within 75-125% of expected value.	Reanalyze once. Verify solution integrity and instrument performance.
Sample Duplicate (D) or Laboratory Fortified Matrix Duplicate (LFMD)	One per 20 field samples of a similar matrix.	All elements at concentrations greater than 10x MDL must be <20% RPD for water and <35% RPD for soil.	Reanalyze sample and duplicate. Reprepare sample and duplicate, if still out, flag data and narrate.

Serial Dilution	One per analytical sequence.	If the analyte conc. >10x MDL after dilution, the concentration in the diluted aliquot should be ±10% of the original analysis.	Reanalyze once. Narrate as a possible chemical or physical interference.
Post-Digestion Spike	If the MS fails.	Analyte should be recovered within 75 - 125% of the expected value.	Reanalyze once. Narrate as a possible matrix effect.

17.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1 Data that fails quality control requirements but cannot be repeated (i.e., insufficient sample volume, or severe matrix effects) should be brought to the immediate attention of the Department or Client Services Representative so that the results may be discussed with the client. A narrative should accompany the analytical results explaining the analytical difficulties the laboratory encountered.

18.0 WASTE MANAGEMENT

18.1 All wastes, extracts, and digests produced by this procedure must be disposed following the procedures outlined in the Chemical Hygiene Plan.

19.0 REFERENCES

19.1 EPA 600/R94-111, Revision 4.4, May 1994, Methods for the Determination of Metals in Environmental Samples, Supplement I [to EPA/600-4-91-010] May 1994.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

20.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

Table 3-
Wavelengths (nm) of Analytical Detectors and Reporting Limits

Element	Wavelength (nm)	Reporting Limit µg/L
Ag	328.0	20
Al	308.2	100
As	189.0	100*
B	182.6	100
Ba	493.4	100
Be	313.0	10*
Ca	317.9	500
Cd	228.8	10*
Co	228.6	50
Cr	267.7	10
Cu	324.7	10
Fe	259.9	100
K	766.4	1,000
Mg	279.0	100
Mn	257.6	10
Mo	202.0	50
Na	588.9	500
Ni	231.6	50
Pb	220.3	100*
Sb	206.8	100*
Se	196.0	100*
SiO_2	288.1	1,070
Sn	189.9	250
Ti	334.9	20
Tl	190.8	100*
V	292.4	50
Zn	213.8	50

* These Reporting Limits do not meet the DLR for reporting drinking waters. These analytes are reported for wastewaters only, drinking waters are run by ICPMS.

INORGANIC ANALYSIS DEPARTMENT
SEQUOIA ANALYTICAL - MORGAN HILL LABORATORY

Table 4-
Concentrations (µg/L) of Analytes in QC Check Solutions

Matrix: 2% HNO_3				
Element	ICV/CCV µg/L	ICSA µg/L	ICSAB µg/L	CRDL µg/L
Ag	5000	-	1000	20
Al	5000	400,000	400,000	-
As	5000	-	1000	100
B	5000	-	-	-
Ba	5000	-	500	100
Be	5000	-	500	10
Ca	5000	400,000	400,000	-
Cd	5000	-	1000	10
Co	5000	-	500	50
Cr	5000	-	500	10
Cu	5000	-	500	10
Fe	5000	400,000	400,000	-
K	50,000	-	-	-
Mg	5000	400,000	400,000	-
Mn	5000	-	500	10
Mo	5000	-	1000	50
Na	25,000	400,000	400,000	-
Ni	5000	-	1000	50
Pb	5000	-	1000	100
Sb	5000	-	1000	100
Se	5000	-	1000	100
SiO_2	2500	-	-	-
Sn	5000	-	-	-
Ti	5000	-	-	-
Tl	5000	-	1000	100
V	5000	-	500	50
Zn	5000	-	1000	50

THOD #: 415.1 Approved for NPDES (Editorial Revision 1974)

ITLE: Organic Carbon, Total (Combustion Or Oxidation)

ALYTE: CAS #

TOC
Total Organic Carbon
C 7440-44-0

NSTRUMENTATION: N/A

ORET No.
Total 00680
Dissolved 00681

.0 Scope and Application

.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.

.2 The method is most applicable to measurement of organic carbon above 1 mg/L.

.0 Summary of Method

.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.

.0 Definitions

.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:

A) soluble, nonvolatile organic carbon; for instance, natural sugars.
B) soluble, volatile organic carbon; for instance, mercaptans.
C) insoluble, partially volatile carbon; for instance, oils.
D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.

.2 The final usefulness of the carbon measurement is in assessing the potential oxygen demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

.0 Sample Handling and Preservation

.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not

show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4-C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified (pH </= 2) with HCl or H2SO4.

5.0 Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6.0 Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7.0 Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 mL.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 mL volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8.0 Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9.0 Precision and Accuracy

1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC, mg/liter	Precision as % mg/liter	Accuracy as TOC, mg/liter	TOC % mg/liter
4.9	3.93	+ 15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Standar

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574-79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

METHOD #: 415.2 (Issued December 1982)

TITLE: Organic Carbon, Total (Low Level) (UV Promoted, Persulfate Oxidation)

ANALYTE:	CAS #
TOC Total Organic Carbon C	7440-44-0

INSTRUMENTATION: Carbon Analyzer

1.0 Scope and Application

1.1 This method covers the determination of total organic carbon in drinking water and other waters subject to the limitations in 1.3 and 5.1 .

1.2 This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method.

1.3 This method is applicable only to the carbonaceous matter which is either soluble or has a particle size of 0.2 mm or less.

1.4 The applicable range is from approximately 50 ug/L to 10 mg/L. Higher concentrations may be determined by sample dilution.

2.0 Summary of Method

A sample is combined with 1 mL of acidified persulfate reagent and placed in a sparger. The sample is purged with helium which transfers inorganic CO2 and purgeable organics to a CO2 scrubber. The CO2 is removed with at least 99.9% efficiency with a 2.5-minute purge. The purgeable organics proceed through a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is measured by a flame ionization detector. The detector signal is integrated and displayed as the concentration of purgeable organic carbon.

The sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeables are converted to CO2 and transferred to a second sparger where a helium purge transfers the CO2 to the reduction system and into the detector. The signal is integrated, added to the purgeable organic carbon value, and displayed as the concentration of total organic carbon:

3.0 Definitions

3.1 Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO2 scrubber. The definition is instrument-condition dependent.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the purgeable organic carbon from the sample containing acidified persulfate reagent and which is converted to CO2 under the instrument conditions.

3.4 The system blank is the value obtained in 8.2 for an irradiated, recirculated reagent distilled water sample.

4.0 Sample Handling and Preservation

4.1 Sampling and storage of samples must be done in glass bottles.

Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics.

4.2 Because of the possibility of oxidation or bacterial decomposition of

some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4-C) and protected from sunlight and atmospheric oxygen.

.3 When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.

.0 Interferences

5.1 If a sample is homogenized to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results.

6.0 Apparatus

.1 Apparatus for blending or homogenizing samples: A household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

.2 Apparatus for Total Organic Carbon: The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator. This method is based on the Dohrmann Envirotech DC-54 Carbon Analyzer. Other instruments having similar performance characteristics may be used.

6.3 Sampling Devices: Any apparatus that will reliably transfer 10 mL of sample to the sparger. A 50 mL glass syringe is recommended when analyzing samples with easily purgeable organics so as to minimize losses.

7.0 Reagents

.1 Reagent Distilled Water: Distilled water used in preparation of standards and for dilution of samples should be ultra-pure to reduce the magnitude of the blank. Carbon dioxide-free, double distilled water is recommended. The water should be distilled from permanganate or be obtained from a system involving distillation and carbon treatment. The reagent distilled water value must be compared to a system blank determined on a recirculated distilled water sample. The total organic carbon value of the reagent distilled water should be less than 60 ug/L. Purgeable organic carbon values of the reagent distilled water should be less than 4 ug/L.

7.2 Potassium hydrogen phthalate, stock solution, 500 mg carbon/liter: Dissolve 1.063 g of potassium hydrogen phthalate (Primary Standard Grade) in reagent distilled water (7.1) and dilute to 1 liter.

.3 Potassium hydrogen phthalate (2 mg/L): Pipet 4 mL of potassium hydrogen phthalate stock solution (7.2) into a one liter volumetric flask and dilute to the mark with reagent distilled water (7.1).

.4 Potassium hydrogen phthalate (5 mg/L): Pipet 1 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.5 Potassium hydrogen phthalate (10 mg/L): Pipet 2 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.6 Acidified Persulfate Reagent: Place 100 mL of reagent distilled water (7.1) in a container. Add 5 g of potassium persulfate. Add 5 g (3 mL) of concentrated (85%) phosphoric acid.

.7 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 mL volumetric flask. Dissolve with reagent distilled water (7.1) and dilute to the mark.

.8 Carbonate-bicarbonate, standard solution 50 mg/L: Place 5 mL of the carbonate-bicarbonate stock solution in a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

.0 Procedure

8.1 Allow at least 30 minutes warm-up time. Leave instrument console on continuously when in daily use, except for the ultraviolet light source, which should be turned off when not in use for more than a few

blank. This value is a function of the total instrument operation and should not vary significantly from previous runs. Reasons for significant changes in the value should be identified.

8.3 Check the effectiveness of the CO_2 scrubber by analyzing the carbonate-bicarbonate standard solution(7.8). Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of the solution. Transfer 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle. No response, or a very minor reading, should be obtained from this solution.

8.4 Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of reagent distilled water (7.1) blank, standards 7.3, 7.4, and 7.5 and the samples.

8.5 Calibrate the analyzer as follows:

8.5.1 Run the reagent distilled water (7.1) and 5.0 mg/L standard (7.4): Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle
Record the meter reading (see 9.1) of the final carbon value for each of the reagent distilled water (7.1) and the standard (7.4). If the meter reading is more than 25% above or below the calculated value of standard 7.4, reanalyze the standard and set the calibration within 25% (8.5.4), reanalyze the system blank, and then begin 8.5.1 again. If the meter reading (see 9.1) is within 25% of the calculated value, continue to next step. The calculated value is defined in 8.5.2.

8.5.2 Calculate the factor for the deviation of the instrument reading (see 9.1) for the standard (7.4) from the calculated value by:

$$\frac{\text{standard reading} - \text{calculated value}}{\text{calculated value}} = \text{FACTOR}$$

where the calculated value is that value obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water (7.1) with which it has been diluted.

8.5.3 Calculate the adjusted reading by:

calculated value + (RDW - (FACTOR X RDW)) = ADJUSTED READING.
where RDW = mean reagent distilled water (7.1) value.

8.5.4 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 8.5.3.

8.6 Analyze the standards 7.3 and 7.5 in order to check the linearity of the instrument at least once each day:

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the standards 7.3 and 7.5.

8.7 Analyze the samples. Transfer 10 mL of sample with reagent to the first sparger and start the analysis cycle.

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the samples.

9.0 Calculations

9.1 The values are read off the final digital readout in ug/L. The system blank reading obtained in 8.2 must be subtracted from all reagent distilled water, standard and sample readings.

10.0 Precision and Accuracy

10.1 In a single laboratory (MERL), using raw river water, centrifuged river water, drinking water. and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from ten replicates were +/-0.13, +/-0.03, +/-0.02, and +/-0.02 mg/L, respectively.

10.2 In a single laboratory (MERL), using potassium hydrogen phthalate in distilled water at concentrations of 5.0 and 1.0 mg/L total organic carbon, recoveries were 80% and 91%, respectively.

11.0 Bibliography

1. Proposed Standard Method for Purgeable and Nonpurgeable Organic Carbon in Water (UV-promoted, persulfate oxidation method). ASTM Committee D-19, Task Group 19.06.02.03 (Chairman R. J. Joyce), January 1978.
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